OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETALDEHYDE

INTRODUCTION

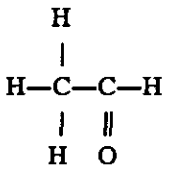
This guideline summarizes pertinent information about acetaldehyde for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

CH_3CHO

- **Structure**



- **Synonyms**

Acetic aldehyde, ethanal, acetylaldehyde, ethyl aldehyde

- **Identifiers**

1. CAS No.: 75-07-0
2. RTECS No.: AB1925000
3. DOT UN: 1089 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

Acetaldehyde is a colorless, flammable, volatile liquid or gas (above 69°F) with a pungent, fruity odor detectable at low concentrations. The odor threshold is reported to be between 0.05 and 2.3 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44.1
2. Boiling point (at 760 mm Hg): 21°C (69.8°F)
3. Specific gravity (water = 1): 0.79 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetaldehyde): 1.5
5. Melting point: -123.5°C (-190.3°F)
6. Vapor pressure at 20°C (68°F): 740 mm Hg
7. Solubility: Miscible with water, alcohol, ether, acetone, benzene, gasoline, solvent naphtha, toluene, turpentine, and xylene
8. Evaporation rate (ether = 1): 3

- **Reactivity**

1. Conditions contributing to instability: Contact of acetaldehyde with air may cause the formation of explosive peroxides, and contact of this substance with heat or flame may cause fires or explosions. Contact with trace metals or alkaline materials may cause acetaldehyde to undergo hazardous polymerization.

2. Incompatibilities: Fire and explosion may result from contact of acetaldehyde with strong oxidizers. Acetaldehyde reacts vigorously with acid anhydrides, alcohols, anhydrous ammonia, amines, ketones, phenols, hydrogen cyanide, hydrogen sulfide, halogens, phosphorus, isocyanates, and strong alkalies.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and methane) may be released in a fire involving acetaldehyde.

4. Special precautions: Liquid acetaldehyde attacks some coatings and some forms of plastic and rubber.

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• **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to acetaldehyde.

1. Flash point: -37.8°C (-36°F) (closed cup)

2. Autoignition temperature: 175°C (347°F)

3. Flammable limits in air (% by volume): Lower, 4.0; upper, 60.0

4. Extinguishant: Use dry chemical, carbon dioxide, or alcohol foam to fight fires involving acetaldehyde. Water may be ineffective, but it may be used to keep fire-exposed containers cool and to protect persons attempting to stop the leak. If a leak or spill of acetaldehyde has not ignited, water spray may be used to disperse vapors.

Fires involving acetaldehyde should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetaldehyde may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetaldehyde. Firefighters' protective clothing may provide limited protection against fires involving acetaldehyde.

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Adminstration (OSHA) permissible exposure limit (PEL) for acetaldehyde is 100 ppm (180 mg/m^3) as an 8-hr TWA concentration and 150 ppm (270 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure which should not be exceeded at any time during the working day [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers acetaldehyde to be a potential occupational carcinogen and recommends exposures be controlled to the lowest feasible limit [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned an acetaldehyde threshold limit value (TLV) of 100 ppm (180 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 150 ppm (270 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of conjunctivitis and sensory irritation of the respiratory tract associated with exposure to acetaldehyde. The NIOSH limit is based on positive carcinogenic results in animal studies.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to acetaldehyde can occur through inhalation, ingestion, or contact with the eyes, skin, or mucous membranes.

• **Summary of toxicology**

1. *Effects on Animals*: Acetaldehyde is an irritant of the eyes, mucous membranes, and upper respiratory tract in animals; at high concentrations, it is a central nervous system depressant. Acetaldehyde has caused squamous cell carcinomas and adenocarcinomas of the nasal cavity in rats and hamsters; it is also embryotoxic and teratogenic in several species of animals. Acetaldehyde causes severe irritation when applied to the eyes of rabbits; it causes mild irritation in contact with skin [NIOSH 1991]. In rats, the oral LD_{50} is 661 mg/kg, and the LC_{50} is 37 g/m^3 (20,550 ppm) for 30 min [NIOSH 1991]. Cats exposed to 380 ppm for 7 hr showed no effects; but increasing the concentration to 1,520 ppm caused signs of respiratory tract irritation [ACGIH 1991a]. Rats exposed to concentrations ranging from 400 to 5,000 ppm for 6 hr/day, 5 days/week for 4 weeks showed slight degeneration of the nasal epithelium at 400 ppm, and growth retardation, increased urinary output (in males only), and slight-to-moderate degeneration (with or without hyperplasia and metaplasia) of the nasal epithelium at 1,000 or 2,200 ppm [IARC 1985]. The rats exposed to 5,000 ppm showed severe growth retardation, increased neutrophil counts, reduced urine volumes, increased lung weights, and severe degenerative hyperplasia and metaplasia of the nasal, laryngeal, and tracheal epithelium [NLM 1992]. Hamsters were exposed to acetaldehyde concentrations ranging from 390 to 4,560 ppm for 6 hr/day, 5 days/week for 90 days. At the lowest concentration, these animals showed no toxic effects; at the highest concentration, however, they showed signs of eye and nose irritation, growth retardation, and erythrocytosis. At autopsy, these high-dose animals showed

increased kidney and heart weights and severe histopathologic changes of the respiratory epithelium [IARC 1985]. Fetal malformations (facial and cranial), digital anomalies, and embryonic deaths (resorptions) occurred in the offspring of rats and mice from dams treated with acetaldehyde during pregnancy [IARC 1985]. Acetaldehyde has been tested for carcinogenicity in rats by inhalation and in hamsters by inhalation and intratracheal administration. In rats, inhalation of acetaldehyde caused a statistically significant increase in the incidence of nasal adenocarcinomas and squamous cell carcinomas of the lungs. In hamsters, inhalation caused a significant increase in the incidence of laryngeal carcinoma, and intratracheal injections resulted in the induction of "peribronchiolar adenomated lesions," which were apparently not classified as tumors. The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence for the carcinogenicity of acetaldehyde in animals [IARC 1987]. Acetaldehyde is mutagenic in bacterial and mammalian test systems with and without activation [NIOSH 1991].

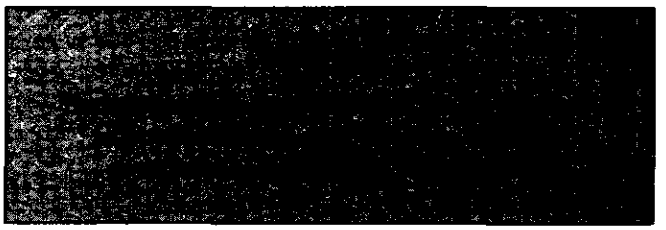
2. *Effects on Humans*: Acetaldehyde is an irritant of the eyes, mucous membranes, skin, and upper respiratory tract, and it is a central nervous system depressant in humans. On the basis of effects seen in animals, acetaldehyde is a potential carcinogen in humans. Although sensitive individuals experienced irritation when exposed to 25 ppm for 15 min, most unacclimated human volunteers exposed to 50 ppm experienced mild eye irritation, and all subjects exposed to 200 ppm developed conjunctivitis [Proctor et al. 1988]. Upper respiratory tract irritation was reported at a vapor concentration of 134 ppm [Proctor et al. 1988]. Eye contact with liquid acetaldehyde causes a burning sensation and superficial corneal injury; exposure to concentrations above 50 ppm may cause persistent tearing, photophobia, and injury to the corneal epithelium [Grant 1986]. Acetaldehyde causes erythema when splashed on the skin; if contact is repeated or prolonged, this substance may cause dermatitis or skin burns [Proctor et al. 1988]. A study of East German workers exposed to acetaldehyde and other chemicals in a chemical factory showed an increase in the number of cancers of the bronchial tubes and oral cavity. However, IARC has concluded that the results of this study are inconclusive because the workers were exposed to other chemicals and only a small, poorly defined population was involved [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acetaldehyde can cause irritation of the eyes with burning, conjunctivitis, tearing, blurred vision, and photophobia; irritation and burning of the nose with rhinorrhea; and irritation of the upper respiratory tract with pain and coughing. Exposure to high levels of this substance may cause headache, drowsiness, dizziness, excitement, and agitation, followed by narcosis or stupor, pulmonary edema, and possibly death resulting from respiratory failure; however, ingestion can also induce nausea, vomiting, and diarrhea. Skin contact may cause dermatitis and burns of the exposed area.

2. *Chronic exposure*: Chronic exposure to acetaldehyde can cause conjunctivitis, coughing, difficult breathing, and dermatitis. On the basis of effects seen in animals, chronic exposure to acetaldehyde may cause heart and kidney damage, embryotoxicity, teratogenic effects, and possibly cancer in humans.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetaldehyde. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetaldehyde are inhaled, move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetaldehyde or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acetaldehyde and may result in worker exposures to this substance:

—Synthesis of acetic acid, acetic anhydride, acrolein, aldol, butanol, butylene glycol, chloral, crotonaldehyde, 2-ethylhexanol, metaldehyde, paraldehyde, pentaerythritol, peracetic acid, pyridines, and trimethylolpropane

—Manufacture of synthetic resins, aniline dyes, herbicides, fungicides, other pesticides, explosives, and pharmaceuticals

—Synthesis of rubber processing chemicals, disinfectants, cosmetics, and perfumes

—Use of acetaldehyde in silvering mirrors and as an alcohol denaturant

—Use of acetaldehyde as a hardening agent in photography and in the manufacture of gelatin, glue, lacquers, varnishes, and casein products

—Use of acetaldehyde as a flavoring agent and additive in milk products and candies and as a preservative for food and leather

The following methods are effective in controlling worker exposures to acetaldehyde, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to acetaldehyde, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetaldehyde at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, and respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetaldehyde exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetaldehyde on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. Acetaldehyde can be detected in the blood, urine, and breath of exposed individuals. However, aldehyde concentrations in these biological specimens have not been correlated with airborne concentrations of this substance. Therefore, no biological monitoring method acceptable for routine use has yet been developed for acetaldehyde.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to acetaldehyde may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetaldehyde is determined by using a silane-treated glass tube that is packed with a 225-mg backup section and a 450-mg sampling section of pretreated XAD-2 adsorbent coated with 10% (by weight) 2-(hydroxymethyl)piperidine. Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 3 liters is collected (8-hr TWA), or they are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 0.75 liter is collected (STEL). Analysis is conducted by gas chromatography using a nitrogen/phosphorus detector. The limit of detection for this procedure is 580 parts per billion. This method is described in the OSHA Computerized Information System [OSHA 1990]. A similar method for sampling and analyzing acetaldehyde is included in Method 2538 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If acetaldehyde contacts the skin, workers should immediately flush the affected areas with large amounts of water and then wash with soap and water.

Clothing and shoes contaminated with acetaldehyde should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of acetaldehyde, particularly its potential for causing skin or eye burns on prolonged contact.

A worker who handles acetaldehyde should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetaldehyde or a solution containing acetaldehyde is handled, processed, or stored.

STORAGE

Acetaldehyde should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Bulk quantities of acetaldehyde should be stored outside in detached, refrigerated tanks that conform to the requirements of the hazard communication standard. Storage in an inert gas atmosphere is recommended. Only nonsparking tools and equipment should be used to handle this OSHA Class IA flammable liquid. Containers of acetaldehyde should be protected from physical damage and should be stored separately from alkaline materials, acids, halogens, alcohols, ammonia, amines, ketones, hydrogen sulfide, hydrogen cyanide, acid anhydrides, phenols, oxidizing agents, and all ignition sources. All electrical service in storage areas should be of explosionproof design. To prevent static sparks, containers and equipment used to transfer acetaldehyde should be electrically grounded and bonded. Because empty containers may contain acetaldehyde residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetaldehyde, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete.

The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Provide maximum explosionproof ventilation to ventilate area of leak or spill.

5. Use nonsparking tools during cleanup.

6. Use water spray to flush spills away from workers and to dilute the spill.

7. Absorb small liquid spills with paper towels, vermiculite, or sand and place the material in a covered container for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the acetaldehyde for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetaldehyde is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for acetaldehyde is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of acetaldehyde per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetaldehyde emitted or released from their facility annually.

- ***Hazardous waste management requirements***

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acetaldehyde is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U001. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Acetaldehyde may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of acetaldehyde are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetaldehyde exceeds

prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent skin contact with acetaldehyde. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acetaldehyde and have demonstrated good-to-excellent resistance: Teflon®, butyl rubber, and polyethylene/ethylene vinyl alcohol. Butyl rubber may provide more than 8 hr of resistance to permeation by acetaldehyde. Natural rubber, neoprene, nitrile rubber, polyethylene, polyvinyl alcohol, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by acetaldehyde.

If acetaldehyde is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Splashproof safety glasses, goggles, or face shields should be worn during operations in which there is any possibility of eye contact with acetaldehyde. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with this substance. Contact lenses should not be worn if the potential exists for acetaldehyde exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETIC ACID

INTRODUCTION

This guideline summarizes pertinent information about acetic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_2H_4O_2$

- **Structure**

CH_3COOH

- **Synonyms**

Ethanoic acid, ethylic acid, glacial acetic acid, methanecarboxylic acid, vinegar acid

- **Identifiers**

1. CAS No.: 64-19-7

2. RTECS No.: AF1225000

3. DOT UN: 2789 29 (glacial acetic acid or acetic acid solutions that are more than 80% acid); DOT UN: 2790 60 (aqueous solutions that are more than 10% but not more than 80% acid)

4. DOT labels: Corrosive, Flammable Liquid (glacial acetic acid or acetic acid solutions that are more than 80% acid); Corrosive (aqueous solutions that are more than 10% but not more than 80% acid)

- **Appearance and odor**

At temperatures above 16.7°C (62°F), acetic acid is a clear, colorless, combustible liquid with a pungent, vinegarlike odor. The odor threshold is reported to be between 0.21 and 1.0 parts per million (ppm) parts of air. This substance is available commercially in strengths ranging from 6% to more than 99% acid, by weight. Glacial acetic acid is 99.4% acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data (glacial acetic acid)**

1. Molecular weight: 60.1

2. Boiling point (at 760 mm Hg): 118°C (244.4°F)

3. Specific gravity (water = 1): 1.05 at 20°C (68°F)

4. Vapor density (air = 1 at boiling point of acetic acid): 2.1

5. Melting point: 16.7°C (62°F)

6. Vapor pressure at 20°C (68°F): 11 mm Hg

7. Solubility: Miscible with water, alcohol, glycerol, carbon tetrachloride, and ether; insoluble in carbon disulfide

8. Evaporation rate (butyl acetate = 1): 1.0

- **Reactivity**

1. Conditions contributing to instability: Heat and freezing temperatures. The vapor of acetic acid forms explosive mixtures with air.

2. Incompatibilities: Fires or explosions may result from contact of acetic acid with chromic acid, ammonium nitrate, sodium peroxide, nitric acid, phosphorus trichloride, or other oxidizers.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released when acetic acid is heated to decomposition.

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National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Special precautions: Acetic acid is highly corrosive in concentrated form; it corrodes metals, some coatings, and some forms of plastic and rubber.

- **Flammability (glacial acetic acid)**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to glacial acetic acid.

1. Flash point: 39°C (103°F) (closed cup). The flash point of concentrated solutions of acetic acid approaches that of glacial acetic acid; dilute acetic acid solutions are not combustible.

2. Autoignition temperature: 427°C (800°F). Dilute acetic acid solutions are not combustible.

3. Flammable limits in air (% by volume): Lower, 4.0; upper, 16.0

4. Extinguishant: Use water spray, dry chemical, alcohol foam, or carbon dioxide to fight fires involving acetic acid. Use water spray to keep fire-exposed containers cool. If a leak or spill has not ignited, water may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving acetic acid should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetic acid may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetic acid. Firefighters' protective clothing may not provide protection against permeation by acetic acid.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetic acid is 10 ppm of air (25 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (25 mg/m^3) as an 8-hr TWA and 15 ppm (37 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetic acid a threshold limit value (TLV) of 10 ppm (25 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 15 ppm (37 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation to the eyes, nose, and respiratory tract associated with exposure to acetic acid.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acetic acid can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: Glacial acetic acid is corrosive to tissues, and concentrated acetic acid solutions (greater than 80% acid) can cause moderate to severe burns. Exposure to the vapors of acetic acid causes eye, skin, mucous membrane, and upper respiratory tract irritation.

When applied to the skin of guinea pigs, acetic acid solutions of 80% or more caused severe burns; concentrations of 50% to 80% caused moderate to severe burns; concentrations of less than 50% caused relatively minor skin damage; and solutions of 10% or less caused no injury [Proctor et al. 1988]. When glacial acetic acid was applied to the eyes of rabbits, it caused immediate and complete destruction; splashes of less concentrated solutions caused less damage [Grant 1986]. The dermal LD_{50} for rabbits was 1,060 mg/kg [NIOSH 1991]. When acetic acid was inhaled, the lowest LC_{50} for mice and guinea pigs exposed for 1 hr was approximately 5,000 ppm [NLM 1991]. Guinea pigs exposed for 1 hr to airborne acetic acid concentrations ranging from 5 to 500 ppm showed an increase in pulmonary flow resistance, a decrease in lung compliance, and an increase in the time constant of the lungs and minute volume [Amdur 1961]. At concentrations above 100 ppm, guinea pigs also showed labored breathing and a decrease in respiratory rate [Amdur 1961]. Mice exposed to acetic acid vapor at approximately

1,000 ppm showed signs of conjunctival and upper respiratory tract irritation [Clayton and Clayton 1981]. The oral LD_{50} in rats was 3,530 mg/kg [NIOSH 1991].

2. *Effects on Humans*: In vapor form, acetic acid is a severe irritant of the eyes, mucous membranes, upper respiratory tract, and skin. In contact with the skin or eyes, acetic acid solutions of 80% or more can be corrosive, causing severe burns of any exposed tissue. Long-term exposure to the vapors of this substance causes chronic bronchitis and other respiratory effects, erosion of tooth enamel, and cracking and darkening of the exposed skin.

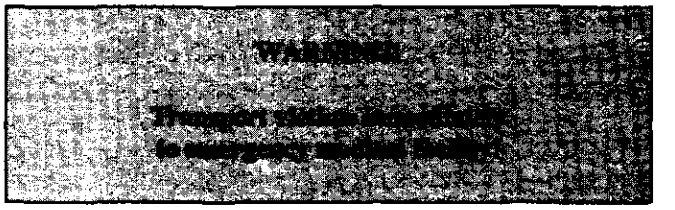
When splashed into the eye, glacial acetic acid has caused permanent corneal opacity; skin contact with glacial acetic acid causes burns and tissue destruction [NLM 1991; AIHA 1978]. Ingestion of corrosive concentrations can cause tissue destruction, perforation, and stricture (delayed) of the throat, esophagus, and stomach; intestinal hemorrhage; and heart and renal damage [NLM 1991]. Unacclimatized individuals have experienced eye irritation at concentrations below 10 ppm, tolerable irritation at 25 ppm, and intolerable eye, nose, and throat irritation at 50 ppm [Proctor et al. 1988]. Exposure at 800 to 1,200 ppm becomes intolerable within 3 min of exposure [ACGIH 1991a]. Five workers who had been exposed to acetic acid vapor at 80 to 200 ppm for 7 to 12 years had thickening and blackening of the skin on the hands, eye inflammation, dental erosion (of both canines and incisors), and chronic pharyngitis and bronchitis [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acetic acid vapor can cause redness, inflammation, lacrimation, runny nose, sore throat, coughing, bronchitis, pulmonary edema, labored breathing, and dyspnea. Death can result from circulatory collapse, renal failure, or glottic edema. Skin contact with concentrated solutions of acetic acid produces redness, blistering, and deep burns; these signs may be delayed for as long as 4 hr after contact. Eye contact with concentrated solutions of acetic acid causes immediate pain and tearing, redness, photophobia, and corneal opacities; if the exposure is severe, vision may be permanently impaired. In addition, ingestion can produce throat, esophageal, and gastric irritation, corrosion, stricture, and perforation; nausea; vomiting; diarrhea; hemorrhage; and shock.

2. *Chronic exposure*: Acetic acid vapors can cause sore throat, coughing, difficult breathing, decrements in pulmonary function, and erosion of the enamel on the incisors and canine teeth. Skin sensitization has rarely been reported. Long-term exposure of the skin to acetic acid vapor may cause it to darken, thicken, and crack.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetic acid! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetic acid are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetic acid or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures

(e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acetic acid and may result in worker exposures to this substance:

—Production of cellulose acetate, vinyl acetate, inorganic acetates, organic acetates (esters), acetic anhydride, chloroacetic acid, ethyl alcohol, ketene, methyl ethyl ketone, acetone, acetanilide, and acetyl chloride

—Use of acetic acid in the dyeing, pharmaceutical, canning, fermentation, and food-preserving industries; in pigment production; and in the tanning of rubber

—Use of acetic acid as a solvent in the liquid-phase oxidation of p-xylene to terephthalic acid, as a fungicide, and as an insecticide

—Use of acetic acid in the production of plastics and photographic chemicals, as a natural latex coagulant, as an oil-well acidizer, in textile printing, as a laundry sour (neutralizer), and as a solvent for gums, resins, volatile oils, and other substances

—Use of acetic acid in the manufacture of Paris green, white lead, and rinse and stain removers

The following methods are effective in controlling worker exposures to acetic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, teeth, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with keratoconjunctivitis or other eye disorders, skin allergies or other skin disorders, erosion of tooth enamel, or respiratory disorders.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employ-

ment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetic acid on the eyes, skin, teeth, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetic acid.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetic acid is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 270 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. The limit of detection for this procedure is 0.01 mg/sample. This method is an OSHA modification of Method 1603 from the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Acetic acid can be absorbed through the skin in toxic amounts, and concentrated solutions of this substance can also cause skin burns. Therefore, if acetic acid contacts the skin, workers should immediately rinse the affected areas with large amounts of water for a minimum of 15 min.

Clothing and shoes contaminated with acetic acid should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the corrosive properties of acetic acid.

A worker who handles acetic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetic acid is handled, processed, or stored.

STORAGE

Acetic acid should be stored in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area should be detached and should be well-ventilated and have acid-resistant floors. The temperature of the storage area should be maintained above 16.7°C (62°F) to prevent rupturing of the containers. Electrical fixtures in the storage area should be vaporproof, and any tools used should be of the nonsparking type. Containers of acetic acid should be protected from physical damage and should be stored separately from oxidizing agents, combustible materials, heat, sparks, and open flame. Because empty containers may contain acetic acid residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. If the vapor from the spill has not ignited, use water spray to reduce the vapors and to protect workers attempting to stop the leak.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the acetic acid for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetic acid is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for acetic acid is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetic acid is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- ***Respiratory protection program***

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent any possibility of skin contact with acetic acid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by acetic acid and may provide protection

for periods greater than 8 hr: butyl rubber, Teflon®, and Saranex®. Materials that may withstand permeation for more than 4 but fewer than 8 hr are neoprene, polyethylene, and polyethylene/ethylene vinyl alcohol. Natural rubber, polyvinyl chloride, and Viton® demonstrated questionable protection against permeation by acetic acid. Nitrile rubber and polyvinyl alcohol have demonstrated poor resistance to permeation by acetic acid.

If acetic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetic acid might contact the eyes (e.g., through splashes of solution). Splashproof, gas-tight goggles may also be required to prevent irritation of the eyes from acetic acid vapor. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetic acid. Contact lenses should not be worn if the potential exists for acetic acid exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETIC ANHYDRIDE

INTRODUCTION

This guideline summarizes pertinent information about acetic anhydride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_6O_3$

- **Structure**

$(CH_3CO)_2O$

- **Synonyms**

Acetanhydride, acetic acid anhydride, acetyl ether, acetic oxide, acetyl oxide, ethanoic anhydride

- **Identifiers**

1. CAS No.: 108-24-7
2. RTECS No.: AK1925000
3. DOT UN: 1715 39
4. DOT labels: Corrosive, Flammable Liquid

- **Appearance and odor**

Acetic anhydride is a colorless liquid with a strong, pungent, vinegarlike odor. The odor threshold is reported to be between 0.13 and 0.34 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.1
2. Boiling point (at 760 mm Hg): 139°C (282°F)
3. Specific gravity (water = 1): 1.08 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetic anhydride): 3.5
5. Melting point: -73°C (-99.4°F)
6. Vapor pressure at 20°C (68.8°F): 4 mm Hg
7. Solubility: Soluble in cold water; decomposes in hot water to form acetic acid; miscible with alcohol, chloroform, ether, and ethyl acetate
8. Evaporation rate (butyl acetate = 1): 0.46

- **Reactivity**

1. Contact of acetic anhydride vapors with water or air should be avoided.
2. Incompatibilities: Fires and explosions may result from contact of acetic anhydride with water, alcohols, strong oxidizers, chromic acid, amines, or strong caustics.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon dioxide, carbon monoxide, various hydrocarbons, and acid aerosols) may be released when acetic anhydride is heated or decomposes.
4. Special precautions: Acetic anhydride attacks some coatings and some forms of plastic and rubber. It is corrosive to iron, steel, and other metals.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to acetic anhydride.

1. Flash point: 49°C (120°F) (closed cup)
2. Autoignition temperature: 316°C (600°F)
3. Flammable limits in air (% by volume): Lower, 2.7; upper, 10.3

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4. Extinguishant: Use carbon dioxide or dry chemical for small fires and alcohol foam for large fires. Water should be used with caution because acetic anhydride reacts with water.

Fires involving acetic anhydride should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetic anhydride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Avoid directing water into containers of acetic anhydride. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetic anhydride. Chemical protective clothing that is specifically recommended for acetic anhydride may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acetic anhydride.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetic anhydride is 5 ppm (20 mg/m^3) as a ceiling limit which should not be exceeded during any part of the workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (20 mg/m^3) as a ceiling limit [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetic anhydride a ceiling limit value of 5 ppm (21 mg/m^3), which should not be exceeded during any part of the working exposure [ACGIH 1991a].

• Rationale for limits

The limits are based on the risk of ocular and respiratory irritation associated with high short-term exposure to acetic anhydride.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to acetic anhydride can occur through inhalation, ingestion, and eye or skin contact. Acetic anhydride also penetrates the skin.

• Summary of toxicology

1. *Effects on Animals*: Acetic anhydride is highly corrosive and causes severe irritation and burns of the eyes, mucous membranes, and skin of exposed animals. When instilled into the eyes, acetic anhydride can be corrosive. It can also penetrate the intact corneal epithelium in concentrations sufficiently high to cause iritis [NLM 1992]. Guinea pigs repeatedly challenged with dermal applications of acetic anhydride developed skin sensitization [Proctor et al. 1988]. The dermal LD_{50} for rabbits is 4,000 mg/kg [NIOSH 1991]. Rats survived exposure to saturated vapors for 5 min [Deichmann and Gerade 1969]. Six rats exposed to 1,000 ppm of acetic anhydride for 4 hr survived, but those inhaling 2,000 ppm for the same interval died [ACGIH 1991b]. The oral LD_{50} for rats is 1,780 mg/kg.

2. *Effects on Humans*: Exposure to acetic anhydride in either the liquid or vapor form causes severe irritation of the eyes, skin, and mucous membranes in humans. Eye contact can lead to corneal burns, erosion, edema, scarring, cataracts with temporary or permanent visual impairment, and inflammation and structural damage of the iris [Grant 1986; Klaassen et al.1986]. In contact with the skin, acetic anhydride causes delayed burns that may be slow to heal [Grayson 1985; Sittig 1985]. The vapor of this substance is reported to be irritating even at a concentration as low as 0.09 ppm [NLM 1992]. Workers exposed to concentrations of acetic anhydride greater than 5 ppm experienced acute eye and upper respiratory tract irritation; their symptoms included severe eye pain and difficult breathing [Proctor et al. 1988]. Inhalation of high concentrations of this substance can cause bronchospasm and ulceration of the nasal mucosa [Proctor et al. 1988]. Humans exposed to the vapor of acetic anhydride occasionally become sensitized to this substance [Proctor et al. 1988]. Ingestion of acetic anhydride can cause corrosion of oral, esophageal, and gastric tissues as well as hemorrhages, strictures, and stenoses but rarely perforations [NLM 1992].

• Signs and symptoms of exposure

1. *Acute exposure*: Acetic anhydride is corrosive to tissues. It can cause a burning sensation in the nose and throat, cough, pain in the chest, difficult breathing, dyspnea, and pulmonary edema. Exposure of the eye to liquid or vaporous acetic anhydride results in excessive tearing, redness, pain, and photophobia. In contact with the skin, acetic anhydride can cause corrosion, burns, and blisters. Ingestion can also induce clammy skin, weak and rapid pulse, nausea, vomiting,

shallow respiration, and decreased urine output. In cases where circulatory collapse has occurred and gone uncorrected for several hours, renal failure and ischemic liver and heart lesions have resulted. Death following ingestion can result from glottic edema or circulatory shock.

2. *Chronic exposure*: Acetic anhydride can cause conjunctivitis, pulmonary edema with coughing and difficult breathing, and skin sensitization with redness, itching, and wheals.

- **Emergency procedures**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of acetic anhydride! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetic anhydride are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetic anhydride or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. *Drinking a carbonated beverage or more than one cup of fluid* could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acetic anhydride and may result in worker exposures to this substance:

—Manufacture of acetyl compounds, cellulose acetate, cellulose esters, chloroacetic acid, acetyl chloride, triacetate fibers, and vinyl acetate

—Processing of dyes, perfumes, explosives, and flavorings

—Electropolishing of metals and processing of semiconductors

—Use of acetic anhydride as an acetylizer and solvent in examining wool fat, glycerol, fatty and volatile oils, and resins, and in detecting rosins

—Use of acetic anhydride as a dehydrating agent in nitrations, sulfonations, and other reactions where removal of water is necessary

—Use of acetic anhydride in the manufacture of pharmaceuticals, including aspirin, and as an intermediate in the synthesis of pesticides

—Use of acetic anhydride as an esterifying agent for food starch

The following methods are effective in controlling worker exposures to acetic anhydride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations must be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetic anhydride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetic anhydride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetic anhydride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetic anhydride on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetic anhydride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetic anhydride is determined by using a standard midget bubbler containing 10 ml of alkaline hydroxylamine hydrochloride solution. The absorbing solution is made up of equal volumes of hydroxylamine hydrochloride (200 g in 1 liter distilled water) and sodium hydroxide (200 g in 1 liter distilled water). The solution is mixed just before use and is stable for only 2 hr. Samples are collected at a recommended flow rate of 0.2 to 1 liter/min until a recommended air volume of 25 to 100 liters is collected. Analysis is performed colorimetrically using

visible absorption spectrophotometry. A purple-colored complex is formed by adding ferric chloride solution to the sample. The limit of detection for this procedure is 0.05 mg/sample. This method is described in Method 3506 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If acetic anhydride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water. Get medical help immediately.

Clothing and shoes contaminated with acetic anhydride should be removed immediately and provisions should be made for safely removing this chemical from these articles. If gross exposure occurs, remove contaminated clothing under a safety shower. Speed in removing the contaminated material from the skin is extremely important. Persons laundering contaminated clothing should be informed about the hazardous properties of acetic anhydride, particularly its potential to be corrosive to the skin.

A worker who handles acetic anhydride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetic anhydride or a solution containing acetic anhydride is handled, processed, or stored.

STORAGE

Acetic anhydride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Inside storage must be in a standard flammable liquids storage room or cabinet. Steel, galvanized tin, tinned iron, copper, or copper alloys should not be used for piping or valves that will be in contact with acetic anhydride. Containers of acetic anhydride should be protected from physical damage and should be separated from water, alcohols, strong oxidizers, chromic acid, amines, strong caustics, heat, sparks, and open flame. Because containers that formerly contained acetic anhydride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetic anhydride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. If the leak or spill has not ignited, water spray may be used to reduce vapors.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal. Wash the site with soda ash solution and flush with plenty of water.
7. For large liquid spills, build dikes far ahead of the spill to contain the acetic anhydride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetic anhydride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for acetic anhydride is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetic anhydride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetic anhydride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetic anhydride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with acetic anhydride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acetic anhydride and have demonstrated protection for more than 4 but fewer than 8 hr: butyl rubber and Teflon®. Polyvinyl chloride, nitrile rubber, Viton®, and natural rubber have all demonstrated poor resistance to permeation by acetic anhydride.

If acetic anhydride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetic anhydride might contact the eyes (e.g., through vapors or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetic anhydride. Contact lenses should not be worn if the potential exists for acetic anhydride exposure.

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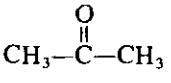
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETONE

INTRODUCTION

This guideline summarizes pertinent information about acetone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_3H_6O
- **Structure:**



- **Synonyms:** Dimethyl ketone, ketone propane, propanone, 2-propanone
- **Identifiers:** CAS 67-64-1; RTECS AL3150000; DOT 1090, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a fragrant, mintlike odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 58.09
2. Boiling point (at 760 mmHg): 56.2 °C (133 °F)
3. Specific gravity (water = 1): 0.79
4. Vapor density (air = 1 at boiling point of acetone): 2.0
5. Melting point: -94.8 °C (-138 °F)
6. Vapor pressure at 20 °C (68 °F): 180.0 mmHg; at 25 °C (77 °F), 226.3 mmHg
7. Miscible in water
8. Evaporation rate (butyl acetate = 1): 6
9. Saturation concentration in air (approximate) at 20 °C (68 °F): 23.7% (237,000 ppm); at 25 °C (77 °F), 29.8% (298,000 ppm)
10. Ionization potential: 9.69 eV

- **Reactivity**

1. Incompatibilities: Contact with acids and oxidizing materials may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., ketene) may be released in a fire involving acetone.
3. Caution: Acetone will dissolve most plastics, resins, and rubber.

- **Flammability**

1. Flash point: -18.0 °C (0 °F) (closed cup)
2. Autoignition temperature: 465 °C (869 °F)
3. Flammable limits in air, % by volume: Lower, 2.2; Upper, 13
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 20 ppm
2. Eye irritation levels: Acetone has been reported to cause a burning sensation of the eyes at a vapor concentration of 500 ppm. Other reports have concluded that irritation in acclimated workers occurs between 1,000 and 1,500 ppm.
3. Evaluation of warning properties for respirator selection: Because of its odor, acetone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetone is 1,000 parts of acetone per million parts of air (ppm) [2,400 milligrams of acetone per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 250 ppm (590 mg/m³) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 750 ppm (1,780 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the (ACGIH) short-term exposure limit (STEL) is 1,000 ppm (2,375 mg/m³) (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for acetone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	1,000	2,400
NIOSH REL TWA	250	590
ACGIH TLV® TWA	750	1,780
STEL	1,000	2,375

HEALTH HAZARD INFORMATION

• Routes of exposure

Acetone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of acetone produced depression of respiration and narcosis in rats. Subchronic dermal application or subcutaneous injection of acetone produced cataracts in guinea pigs.

2. *Effects on humans:* Acute inhalation of acetone has produced narcosis, and repeated exposures have caused inflammation of the respiratory tract, stomach, and small intestine. Studies of persons clinically exposed indicate that acetone is metabolized slowly and may accumulate in the body throughout a 40-hour workweek.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to acetone can cause eye irritation, dryness of the mouth and throat, nausea, vomiting, headache, sleepiness, dizziness, light-headedness, weakness, incoordination, loss of energy, fainting, and unconsciousness.

2. *Long-term (chronic):* Exposure to acetone can cause dizziness and sleepiness. Dryness, irritation, and inflammation of skin can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to acetone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, eyes, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to acetone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to acetone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, eyes, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to acetone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting acetone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure acetone may also be used if available. A detailed sampling and analytical method for acetone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with acetone.

Workers should be provided with and required to use splash-proof safety goggles where acetone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with acetone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of acetone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of acetone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with acetone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle acetone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to acetone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for acetone

Operations	Controls
During application of lacquer, paints, and varnishes	Natural ventilation, local exhaust ventilation, workroom ventilation, personal protective equipment
During use of solvents and cementing agents	Personal protective equipment
During dip application of protective coatings; during cleaning operations	Local exhaust ventilation, personal protective equipment
During fabric coating and dyeing processes	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to acetone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If acetone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to acetone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If acetone gets on the skin, wash it immediately with soap and water. If acetone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. If irritation persists after washing, get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

In cases in which environmental levels exceed the NIOSH REL, workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If acetone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing acetone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from acetone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing acetone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Acetone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing acetone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for acetone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with organic vapor cartridge(s)
	Any powered air-purifying respirator with organic vapor cartridge(s)
	Any supplied-air respirator
	Any self-contained breathing apparatus
Less than or equal to 6,250 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 12,500 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any supplied-air respirator with a full facepiece
	Any self-contained breathing apparatus with a full facepiece
Less than or equal to 20,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 20,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 250 ppm (590 mg/m³) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETONITRILE

INTRODUCTION

This guideline summarizes pertinent information about acetonitrile for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_2H_3N

- **Structure**

CH_3CN

- **Synonyms**

Methyl cyanide, cyanomethane, ethanenitrile, ethyl nitrile, methanecarbonitrile

- **Identifiers**

1. CAS No.: 75-05-8
2. RTECS No.: AL7700000
3. DOT UN: 1648 28
4. DOT labels: Flammable Liquid and Poison

- **Appearance and odor**

Acetonitrile is a flammable, colorless liquid with an aromatic odor. The odor threshold is reported to be 40 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 41
2. Boiling point (at 760 mm Hg): 81.6°C (178.9°F)
3. Specific gravity (water = 1): 0.79 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetonitrile): 1.42
5. Melting point: -45°C (-49°F)
6. Vapor pressure at 20°C (68°F): 73 mm Hg
7. Solubility: Miscible with water, methanol, methyl acetate, ethyl acetate, alcohol, ethanol, acetone, acetamide solutions, carbon tetrachloride, chloroform, ethylene chloride, and many unsaturated hydrocarbons
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame. Vapors form explosive mixtures with air.
2. Incompatibilities: Fire and explosion may result from contact of acetonitrile with perchloric acid, iron (III) salts of perchlorate, nitric acid, oleum, indium, nitrating agents, perfluorourea, chlorosulfonic acid, or other strong oxidizers.
3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen, carbon monoxide, carbon dioxide, and hydrogen cyanide) may be released in a fire involving acetonitrile.
4. Special precautions: Liquid acetonitrile attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to acetonitrile.

1. Flash point: 5.6°C (42°F) (closed cup)
2. Autoignition temperature: 523.9°C (975°F)
3. Flammable limits in air (% by volume): Lower, 4.4; upper, 16.0

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use carbon dioxide, dry chemical, or foams on fires involving acetonitrile. Never direct a stream of water into burning pools of liquid acetonitrile because this may scatter and spread the flames. Water spray may be used to cool containers or to protect persons attempting to stop the leak.

Fires involving acetonitrile should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acetonitrile may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetonitrile. Chemical protective clothing that is specifically recommended for acetonitrile may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acetonitrile.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetonitrile is 40 ppm (70 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 60 ppm (105 mg/m^3) as a short-term exposure limit (STEL) [29 CFR 1910.1000, Table Z-1-A]. A STEL is a 15-min TWA exposure that should not be exceeded at any time during the workday.

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 20 ppm (34 mg/m^3) as a TWA for up to a 10-hr workshift and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetonitrile a threshold limit value (TLV) of 40 ppm (67 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 60 ppm (101 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risks of organic cyanide poisoning and liver and respiratory tract injuries associated with exposure to acetonitrile.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to acetonitrile can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Acetonitrile can induce methemoglobinemia and cyanosis because it is metabolized in the body to cyanide. The 8-hr LC_{50} in rats is 7,500 ppm [NIOSH 1991]. The dermal LD_{50} in rabbits is 1,250 mg/kg [NIOSH 1991]. Acutely poisoned animals convulsed and became prostrate before death; autopsy of these animals revealed pulmonary hemorrhage [Proctor et al. 1988]. In mice exposed to 200 or 400 ppm for 6.5 hr/day, 5 days/week for 13 weeks, an increase in liver weight and pathological changes in liver cells were seen at autopsy; signs of anemia were also seen in the high-dose groups before death [ACGIH 1991a]. Dogs and monkeys exposed to a 350-ppm concentration for 7 hr/day, 3 days/week for 13 weeks showed signs of emphysema and other reactive changes in the lungs at autopsy; the monkeys also exhibited brain hemorrhage [Clayton and Clayton 1982]. The oral LD_{50} in rats is 2,730 mg/kg. Teratogenic and embryotoxic effects occurred in hamsters inhaling 5,000 or 8,000 ppm for 1 hr on day 8 of gestation, and a single oral or intraperitoneal dose of 100 to 400 mg/kg also resulted in teratogenic effects in the offspring of exposed rats [ACGIH 1991a].

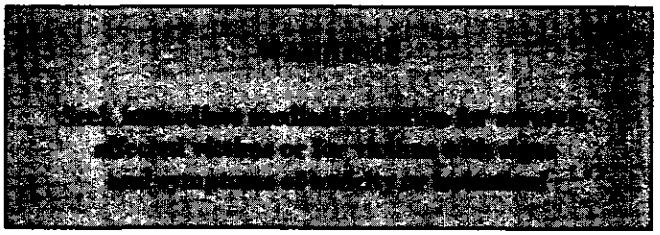
2. *Effects on Humans*: Acetonitrile is a primary irritant of the eyes, mucous membranes, skin, and upper respiratory tract of exposed workers; it has also caused methemoglobinemia and death in humans acutely overexposed. Two volunteers experienced no ill effects after inhaling 80 ppm for 4 hr; however, one of these individuals experienced bronchial irritation after an exposure to 160 ppm for the same interval [Proctor et al. 1988]. Ten painters developed signs of systemic toxicity when exposed to the vapor of a mixture containing 30% to 40% acetonitrile for 2 workdays. Four of the ten printers required hospitalization. One painter died after experiencing massive hematemesis [Proctor et al. 1988]. Several other industrial fatalities have occurred as a result of acute overexposure to acetonitrile. The lowest oral dose toxic in humans is 570 mg/kg; ingestion of this amount of acetonitrile caused gastrointestinal tract disturbances [NIOSH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acetonitrile poisoning can cause flushing or ashen-grey color; chest tightness; headache; nausea; vomiting (with or without blood); sweating; excess saliva production; lassitude; muscle weakness; painful, difficult, or irregular breathing; convulsions; stupor; coma; and cardiac and respiratory arrest.

2. *Chronic exposure*: No signs or symptoms of chronic exposure have been reported.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetonitrile. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetonitrile are inhaled, move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Do ***not*** induce vomiting.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of acetonitrile may result in worker exposures to this substance:

—Use as a solvent for extractive distillation in the manufacture of butadiene and isoprene

—Use as an extractive solvent in separation of fatty acids from fish liver oils; to remove phenol, tar, and color from petroleum hydrocarbons; to recover various alcohols, acids, and dark wood rosins; and in chemical analysis

—Use as a solvent and reactive medium for the preparation of pharmaceuticals, waterproofing compounds, antistatic agents, detergents, polymers, dyestuff intermediates, and for chemical research

—Use as an indifferent medium in physiochemical investigation and in separation of alkaloids in tissue extraction

—Use as a solvent for recrystallization and purification of salts, metals, and steroids; as a spinning solvent for synthetic fibers; as a solvent for epoxy resin coatings

—Use in organic synthesis in preparation of vitamins, perfumes, water softeners, and plasticizers, and as a catalyst to promote ionization reactions

The following methods are effective in controlling worker exposures to acetonitrile, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and

workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations must be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetonitrile, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver and kidneys and of the cardiovascular, respiratory, and central nervous systems. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetonitrile at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with liver, kidney, cardiovascular, respiratory, or central nervous system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetonitrile exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetonitrile on the liver, kidneys, and cardiovascular, respiratory, and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Acetonitrile exposure can be monitored by measurement of its metabolites, cyanide and thiocyanate, in the blood or in plasma and urine, respectively. Some sources suggest that blood cyanide levels of 0.1 mg/l or plasma or urine thiocyanate levels above 20 mg/l indicate excessive exposure. Because smokers often have higher levels of both metabolites, pre-exposure baseline measurements are suggested to establish each worker's baseline level.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetonitrile is determined by using coconut shell charcoal tubes (400/200-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 25 liters is collected. The sample is then treated with benzene to extract the acetonitrile. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method 1606 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Clothing and shoes contaminated with acetonitrile should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Work clothing should not be taken home for laundering. Persons laundering contaminated clothing should be informed about the hazardous properties of acetonitrile, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles acetonitrile should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetonitrile or a solution containing this substance is handled, processed, or stored.

STORAGE

Acetonitrile should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage must be in a standard flammable liquids storage area. All electrical service in the storage area should meet code requirements for flammable atmospheres. Containers of acetonitrile should be protected from physical damage and should be stored separately from perchloric acid, iron (III) salts of perchlorate, nitric acid, oleum, indium, nitrating agents, perfluorourea, chlorosulfonic acid, other strong oxidizers, heat, sparks, and open flame. To prevent static sparks, conveying equipment and storage containers should be electrically grounded and bonded during transfer. Because containers that formerly contained acetonitrile may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetonitrile, persons not wearing protective equipment and clothing should be restricted from contaminated areas until the cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Isolate and ventilate the area of the spill or leak.

5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered, vapor-tight container for later disposal.

6. Large quantities of acetonitrile can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetonitrile is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for acetonitrile is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of this substance per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetonitrile emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acetonitrile is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U003. This substance has been banned from land dis-

posal and may be treated by incineration. Acetonitrile also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetonitrile exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves, boots, aprons, and gauntlets should be worn as necessary to prevent skin contact either with the vapor or the liquid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acetonitrile and have demonstrated good-to-excellent resistance for periods of at least 8 hr: butyl rubber, polyvinyl alcohol, and Teflon®. Natural rubber, neoprene, nitrile, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation.

If acetonitrile is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetonitrile might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetonitrile. Contact lenses should not be worn if the potential exists for acetonitrile exposure.

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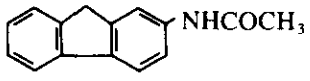
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-ACETYLAMINOFLUORENE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 2-acetylaminofluorene for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{15}H_{13}NO$
- **Structure:** 

- **Synonyms:** 2-AAF; 2-acetamidofluorene; 2-acetaminofluorene; N-acetyl-2-aminofluorene; 2-(acetylamino)fluorene; N-FAA; 2-FAA
- **Identifiers:** CAS 53-96-3; RTECS AB9450000; DOT not assigned
- **Appearance:** Tan, crystalline solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 223.29
2. Melting point: 194°C (381.2°F)
3. Insoluble in water

- **Flammability**

Extinguishant: Dry chemical, carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 2-acetylaminofluorene; however, the OSHA standard requires implementation of stringent controls wherever 2-acetylaminofluorene or solid or liquid mixtures containing at least 0.1% by weight or volume of 2-acetylaminofluorene are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1014, 2-Acetylaminofluorene. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) does not have an assigned threshold limit value (TLV®) for 2-acetylaminofluorene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Acetylaminofluorene may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Subchronic or chronic oral administration of 2-acetylaminofluorene in dogs, rats, or hamsters produced cancers of the bladder or liver. In rats, cancers of the kidneys, pancreas, pelvis, salivary glands, eyes, ear ducts, and auditory and sebaceous glands were also found. In all animals that developed cancer from exposure to 2-acetylaminofluorene, the potent carcinogenic metabolite N-hydroxy-2-acetylaminofluorene was produced. Single oral doses of 2-acetylaminofluorene to pregnant rats on days 8-12 of gestation induced fetal malformations (hydrocephaly).
2. *Effects on humans:* Five cancer patients treated with single oral doses of 2-acetylaminofluorene produced the N-hydroxy-2-acetylaminofluorene metabolite, indicating that 2-acetylaminofluorene may be metabolized in humans as it was in animals that developed cancer from exposure to 2-acetylaminofluorene.

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RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to 2-acetylaminofluorene, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, liver, urinary tract, and reproductive system.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-acetylaminofluorene. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 2-acetylaminofluorene. Because the metabolite N-hydroxy-2-acetylaminofluorene has been identified in both animals and humans administered 2-acetylaminofluorene, consideration should be given to monitoring for this metabolite in workers who may be exposed to 2-acetylaminofluorene.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 2-acetylaminofluorene may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• Method

There is no NIOSH-validated sampling or analytical method for 2-acetylaminofluorene.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory type hoods" or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting

the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system. If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 2-acetylaminofluorene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 2-acetylaminofluorene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-acetylaminofluorene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 2-acetylaminofluorene from materials and equipment. Contaminated materials should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1014:

Areas where 2-acetylaminofluorene is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 2-acetylaminofluorene, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 2-acetylaminofluorene which are not in an isolated system, laboratory type hood, or other system affording equivalent protection against the entry of 2-acetylaminofluorene into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory type hoods" or in locations where 2-acetylaminofluorene is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 2-acetylaminofluorene shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 2-acetylaminofluorene from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-acetylaminofluorene may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 2-acetylaminofluorene

Operation	Controls
During use in research and labortatory facilities	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 2-acetylaminofluorene, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• **Eye exposure**
Where there is any possibility of a worker's eyes being exposed to 2-acetylaminofluorene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-acetylaminofluorene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**
Where there is any possibility of a worker's body being exposed to 2-acetylaminofluorene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use. If 2-acetylaminofluorene gets on the skin, wash it immediately with soap and water. If 2-acetylaminofluorene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**
If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 2-acetylaminofluorene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, 2-acetylaminofluorene may be collected and placed in an appropriate container.
3. For small quantities of liquids containing 2-acetylaminofluorene, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing 2-acetylaminofluorene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. 2-acetylaminofluorene dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container. Dry sweeping and dry mopping of 2-acetylaminofluorene are prohibited by OSHA.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 2-acetylaminofluorene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETYLENE TETRABROMIDE

INTRODUCTION

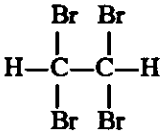
This guideline summarizes pertinent information about acetylene tetrabromide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CHBr_2CHBr_2$

- **Structure**



- **Synonyms**

Tetrabromacetylene, tetrabromoethane; symmetrical tetrabromoethane; 1,1,2,2-tetrabromoethane (TBE); Muthmann's liquid

- **Identifiers**

1. CAS No.: 79-27-6
2. RTECS No.: KI8225000
3. DOT UN: 2504 58
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

Acetylene tetrabromide is a noncombustible, heavy, pale yellow liquid with a pungent, camphorlike odor. No quantitative data is available on the odor threshold.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 345.7
2. Boiling point (at 760 mm Hg): 239°C (462.2°F)
3. Specific gravity (water = 1): 2.96 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acetylene tetrabromide): 11.9
5. Melting point: 0°C (32°F)
6. Vapor pressure at 20°C (68°F): 0.02 mm Hg
7. Solubility: Insoluble in water; miscible with alcohol, chloroform, ether, aniline, glacial acetic acid; soluble in acetone and benzene.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Toxic vapors may result from contact with chemically active metals or strong caustics, or with hot iron, aluminum, or zinc in the presence of steam.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide, carbonyl bromide, brominated solvents, and carbon monoxide) may be released when acetylene tetrabromide decomposes.
4. Special precautions: Acetylene tetrabromide softens or destroys most plastics and rubbers.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to acetylene tetrabromide; this substance is not combustible.

1. Flash point: -18°C (0°F) (closed cup)
2. Autoignition temperature: 335°C (635°F)
3. Flammable limits in air: Not applicable

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4. Extinguishant: Use water to cool containers of acetylene tetrabromide that are involved in a fire.

Fires involving acetylene tetrabromide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acetylene tetrabromide. Chemical protective clothing that is specifically recommended for acetylene tetrabromide may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acetylene tetrabromide.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetylene tetrabromide is 1 ppm (14 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for acetylene tetrabromide [NIOSH 1988, 1991].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetylene tetrabromide a threshold limit value (TLV) of 1 ppm (15 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The OSHA and ACGIH limits are based on the risk of hepatotoxic effects associated with exposure to acetylene tetrabromide.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to acetylene tetrabromide can occur through inhalation of the vapors, ingestion of the liquid, and eye or skin contact with the liquid or vapors.

• Summary of toxicology

1. *Effects on Animals*: Acetylene tetrabromide is a central nervous system depressant and a liver, kidney, and lung toxin in animals. When instilled into the eyes of rabbits, the liquid caused slight conjunctival and superficial corneal injury; on the skin of rabbits, a 24-hr application of 500 mg caused a moderate degree of irritation [NIOSH 1991]. The dermal LD_{50} in rats is 5,250 mg/kg [NIOSH 1991]. The inhalation LC_{50} in rats has been reported as 39 ppm (549 mg/m^3) [NIOSH 1991]. Although no noteworthy effects were described for rats, rabbits, and guinea pigs exposed to saturated vapors (unquantified) for up to 2 hr, 3-hr exposures produced respiratory tract irritation, tremors, and CNS depression (ataxia, loss of the righting reflex, and unconsciousness). Only the guinea pigs died, each having postmortem fatty degeneration of the hepatic and renal parenchyma. The tissues for all survivors from the four species appeared histologically normal [Gray 1950]. Female rats exposed to saturated vapors (~14 ppm at 23°C) for 7 hr did not die and had very slight eye and nasal irritation [Hollingsworth et al. 1963]. The oral LD_{50} in rats is 1,100 mg/kg [NIOSH 1991]. In a subchronic study, rats, rabbits, mice, and a monkey were exposed to ambient concentrations of 1, 4, or 14 ppm for 7 hr/day, 5 days/week for approximately 28, 26, or 15 weeks, respectively. The no observable effect level (NOEL) was 1 ppm. The 4-ppm concentration induced slight lung hemorrhage, congestion, edema, slight hepatocellular centrolobular fatty degeneration, and slight swelling of the renal convoluted tubules. Similar pulmonary and liver changes were reported at 14 ppm [Hollingsworth 1963]. Application of 15 mg to the skin of mice, followed 14 days later with a tumor-promoting agent (phorbol myristate acetate) caused a statistically significant increase in forestomach papillomas [Van Duuren et al. 1979; Proctor et al. 1988; NLM 1991].

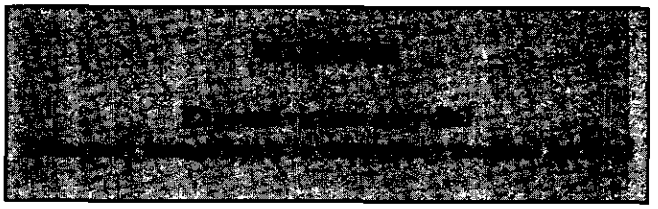
2. *Effects on Humans*: Acetylene tetrabromide is a central nervous system depressant and a liver toxin in humans. When a chemist was exposed to this substance for 7.5 hr at an estimated concentration of 1 to 2 ppm with a single 10-min peak exposure to 16 ppm, he experienced headache, anorexia, nausea, vomiting, and abdominal pain. During a 9-week hospitalization, clinical studies revealed icterus, urobilinuria, bilirubinuria, and severe and nearly fatal liver damage [Proctor et al. 1988; Clayton and Clayton 1981]. Skin absorption of acetylene tetrabromide may also have been involved in this episode of acute poisoning [Proctor et al. 1988; ACGIH 1991a].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to acetylene tetrabromide can cause irritation of the eyes, nose, and upper respiratory tract; headache; nausea; vomiting; anorexia; abdominal pain; ataxia; CNS depression; and death. Jaundice, urobilinuria, bilirubinuria, and monocytosis have also been reported. Exposure to the eyes or skin with liquid acetylene tetrabromide may cause pain, redness, and a slight but reversible conjunctival irritation and corneal injury.

2. *Chronic exposure*: On the basis of effects seen in animals, exposure to acetylene tetrabromide can cause liver, kidney, and lung damage.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of acetylene tetrabromide. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acetylene tetrabromide are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose to remove residues from nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acetylene tetrabromide or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of acetylene tetrabromide may result in worker exposures to this substance:

—Use as a catalyst or catalytic initiator in manufacture of terephthalic acid and synthetic fibers and as a polymer additive in flameproof, flame-retardant polystyrenes, polyurethanes, and polyolefins

—*Use in the density separation of mineral salts*

—Use as a mercury substitute in gauges, as a level indicator in sight gauges, and as a refractive index liquid in microscopy

—Use as a solvent for fats, oils, and waxes

—Use as an ore flotation agent

The following methods are effective in controlling worker exposures to acetylene tetrabromide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers

for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetylene tetrabromide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetylene tetrabromide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with impaired liver function.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetylene tetrabromide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetylene tetrabromide on the eyes, skin, upper respiratory tract, liver, and kidneys. Liver function studies should be performed on a routine basis, particularly in workers exposed to acetylene tetrabromide levels near the PEL. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetylene tetrabromide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetylene tetrabromide is determined by using a silica gel absorption tube (150/75-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 100 liters is collected. The sample is then treated with tetrahydrofuran to extract the acetylene tetrabromide. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.16. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 2003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If acetylene tetrabromide contacts the skin, workers should immediately wash the affected areas thoroughly with soap and water.

Clothing and shoes contaminated with acetylene tetrabromide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of acetylene tetrabromide.

A worker who handles acetylene tetrabromide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetylene tetrabromide is handled, processed, or stored.

STORAGE

Acetylene tetrabromide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of acetylene tetrabromide should be protected from physical damage and should be stored separately from chemically active metals and strong caustics, heat, sparks, and open flame. Because empty containers may contain acetylene tetrabromide residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetylene tetrabromide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. If feasible, remove leaking containers to a safe place.
4. Ventilate atmosphere to reduce vapors.
5. Absorb small spills with sand, vermiculite, or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the acetylene tetrabromide for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetylene tetrabromide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center about an accidental release of acetylene tetrabromide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the annual amount of acetylene tetrabromide emitted or released from their facility.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetylene tetrabromide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetylene tetrabromide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel,

fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with acetylene tetrabromide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Such clothing may include gloves with long sleeves, aprons, footwear, and face shields. No reports have been published on the resistance of various protective clothing materials to permeation by acetylene tetrabromide; however, Viton®, Teflon®, and polyvinyl alcohol materials have been tested against permeation by a similar compound (ethylene dibromide) and have been found to provide good-to-excellent protection. These materials provided more than 8 hr of resistance to permeation by ethylene dibromide. Since specific test data are not available for acetylene tetrabromide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to acetylene tetrabromide.

If acetylene tetrabromide is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Chemical safety glasses, goggles, or face shields should be worn during operations in which acetylene tetrabromide might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetylene tetrabromide. Contact lenses should not be worn if the potential exists for acetylene tetrabromide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACETYLSALICYLIC ACID

INTRODUCTION

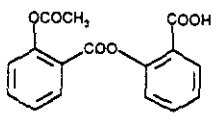
This guideline summarizes pertinent information about acetylsalicylic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CH_3COOC_6H_4COOH$

- **Structure**



- **Synonyms**

Aspirin, ASA, acetol, salicylic acid acetate, 2-acetoxybenzoic acid, acetophen, acetosalic acid, acetal, acetylin, acetylsal, acidum acetylsalicylicum, Asagran, Aspirdrops, Entericin, Caprin, Colfarit, Duramax, Empirin, Measurin, Novid, Rhodine, Saletin, Solpyron

- **Identifiers**

1. CAS No.: 50-78-2
2. RTECS No.: VO0700000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Acetylsalicylic acid is a noncombustible, crystalline, colorless to white powder. This substance is odorless; on contact with moisture, it develops the vinegarlike odor of acetic acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 180.2
2. Boiling point (at 760 mm Hg): 140°C (284°F) (decomposes)
3. Specific gravity (water = 1): 1.4 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 135°C (275°F)
6. Vapor pressure at 20°C (68°F): Negligible
7. Solubility: Soluble in water, alcohol, chloroform, and ether; less soluble in absolute ether
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Fires or explosions may result from contact of acetylsalicylic acid with strong oxidizers. Contact with alkali hydroxides or carbonates may cause decomposition.
3. Hazardous decomposition products: When heated to decomposition, toxic vapors and gases (such as partially oxidized hydrocarbons, carbon monoxide, and carbon dioxide) may be released.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to acetylsalicylic acid; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Acetylsalicylic acid will not burn. Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Dispersed in air, the dust of acetylsalicylic acid is a serious explosion hazard. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires resulting from acetylsalicylic acid explosions.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acetylsalicylic acid is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for acetylsalicylic acid of 5 mg/m^3 as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acetylsalicylic acid a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of respiratory and gastric irritation associated with exposure to acetylsalicylic acid.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to acetylsalicylic acid can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Acetylsalicylic acid can damage the stomach lining and interfere with blood clotting; it is also fetotoxic and teratogenic in animals [Klaassen et al. 1986; NIOSH 1991]. Cats were orally administered total daily doses of either 33 to 63 mg/kg or 81 to 130 mg/kg for up to 35 days. The lowest dose induced toxic hepatitis in the treated animals, but both doses induced anorexia, weight loss, vomiting, depression, and death. Only animals receiving the high doses had hyperpnea (increased rate and depth of breathing), hyperthermia, and disturbances in their acid-base balance [NLM 1991]. Dogs administered oral daily doses of 100 to 300 mg/kg for 1 to 4 weeks vomited bloody emesis and had gastritis and gastric perforations [NLM 1991]. The oral LD_{50} in rats ranges from 1,360 to 1,750 mg/kg [NLM 1991]. Acetylsalicylic acid has been shown to be a developmental toxin in five species of animals; this substance also causes reproductive effects in both males and females [NIOSH 1991]. Teratogenic effects occurred when 125 mg/kg acetylsalicylic acid was administered orally to rats on day 12 of pregnancy; damage to the testes, epididymis, and sperm duct was observed in male rats dosed orally with 2.1 g/kg acetylsalicylic acid for 14 days [NIOSH 1991]. When administered orally or subcutaneously to pregnant rats, mice, rabbits, cats, and dogs, acetylsalicylic acid was fetotoxic or teratogenic [NIOSH 1991]. Chronic administration of a 300-mg/kg dose of acetylsalicylic acid inhibited ovulation in rats by depressing prostaglandin synthesis [NLM 1991].

2. *Effects on Humans*: In the occupational environment, acetylsalicylic acid is a systemic allergen and an irritant of the eyes, mucous membranes, upper respiratory tract, and skin. When in contact with the eyes, this substance causes irritation, conjunctival ulceration, and corneal injury [ACGIH 1991a; Grant 1986]. Aspirin-intolerant individuals develop hives, rhinorrhea, and bronchospasm when exposed to this substance; some persons (e.g., those who are glucose-6-phosphate dehydrogenase deficient) may be especially sensitive to aspirin's effects [Klaassen et al. 1986; Gosselin et al. 1984]. Ingestion of acetylsalicylic acid causes an increased tendency to bleed by interfering with platelet aggregation; this effect has been seen after the ingestion of as little as 150 mg of acetylsalicylic acid [ACGIH 1991a]. Acetylsalicylic acid produces an allergy-like response in about 0.2% of individuals; although aspirin intolerance mimics a true allergic response, this reaction is not believed to be immunologically based [Klaassen et al. 1986].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to acetylsalicylic acid can cause redness and tearing of the eyes, runny nose, scratchy throat, and redness and swelling of the skin.

2. *Chronic exposure*: Chronic exposure to acetylsalicylic acid can cause headache, dizziness, and ringing in the ears; in aspirin-intolerant individuals, it can induce pseudoallergic responses (hives, runny nose, wheezing, and difficult breathing) and a permanent intolerance to this substance. Ingestion of aspirin may lead to an increase in clotting time.

• Emergency procedures

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. Wash contaminated skin with soap and water.

3. *Inhalation exposure*: If a large amount of acetylsalicylic acid is inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if a large amount of acetylsalicylic acid is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The manufacture, handling, and packaging of aspirin tablets or related pharmaceutical products may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to acetylsalicylic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acetylsalicylic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and upper respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific

job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acetylsalicylic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with drug allergies or aspirin intolerance or of diseases of the eyes, skin, or upper respiratory system; individuals using anticoagulant medications may also be at increased risk.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acetylsalicylic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acetylsalicylic acid on the eyes, skin, or upper respiratory tract or on blood clotting time. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acetylsalicylic acid.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acetylsalicylic acid is determined by using a 37-mm glass fiber filter. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 120 liters is collected. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If acetylsalicylic acid contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with acetylsalicylic acid should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles acetylsalicylic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acetylsalicylic acid or a solution containing acetylsalicylic acid is handled, processed, or stored.

STORAGE

Acetylsalicylic acid should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of acetylsalicylic acid should be protected from physical damage and should be stored separately from strong oxidizers, alkali hydroxides, carbonates, moisture, and heat. Because containers that formerly contained acetylsalicylic acid may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acetylsalicylic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Collect spilled material in the most convenient and safe manner and place the material in a covered container for reclamation or later disposal in an approved facility.

2. Absorb liquid containing acetylsalicylic acid in vermiculite, dry sand, earth, or similar material.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acetylsalicylic acid is not subject to EPA emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of acetylsalicylic acid; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acetylsalicylic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acetylsalicylic acid is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acetylsalicylic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with acetylsalicylic acid; protective gloves are recommended when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to acetylsalicylic acid permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to acetylsalicylic acid.

If acetylsalicylic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acetylsalicylic acid might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acetylsalicylic acid. Contact lenses should not be worn if the potential exists for acetylsalicylic acid exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACROLEIN

INTRODUCTION

This guideline summarizes pertinent information about acrolein for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_3H_4O

- **Structure**

$CH_2{=}CHCHO$

- **Synonyms**

Acraldehyde, acrylic aldehyde, acrylaldehyde, trans-acrolein, allyl aldehyde, propenal, 2-propenal, propylene aldehyde, ethylene aldehyde, Aqualine, Biocide, Crolean, Magnacide

- **Identifiers**

1. CAS No.: 107-02-8
2. RTECS No.: AS1050000
3. DOT UN: 1092 30 (inhibited form)
4. DOT labels: Flammable Liquid, Poison (for the inhibited form)

- **Appearance and odor**

Acrolein is a clear, colorless to yellow, flammable liquid with a disagreeable, choking odor. The odor threshold is reported to be between 0.02 and 0.4 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 56.1
2. Boiling point (760 mm Hg): 52.5°C (126.5°F)
3. Specific gravity (water = 1): 0.84 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acrolein): 1.94
5. Melting point: -87.7°C (-125.9°F)
6. Vapor pressure at 20°C (68°F): 210 mm Hg
7. Solubility: Soluble in water, alcohol, ether, and acetone
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame. The vapors of acrolein form explosive mixtures with air.

2. Incompatibilities: Acrolein is very reactive and polymerizes rapidly and violently in the presence of strong acid or basic catalysts, light, heat, and volatile amines. Upon storage, it forms shock-sensitive and heat-sensitive explosive compounds. Fire and explosions may result from contact of acrolein with oxidizers, acids, alkalies, or ammonia.

3. Hazardous decomposition products: Toxic gases and vapors, including peroxides and oxides of carbon, may be released in a fire involving acrolein.

4. Special precautions: An inhibitor, usually hydroquinone, should be added to this highly unstable material to prevent self-polymerization.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to acrolein.

1. Flash point: -26°C (-15°F) (closed cup)
2. Autoignition temperature: 220°C (428°F)
3. Flammable limits in air (% by volume): Lower, 2.8; upper, 31

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use carbon dioxide, dry chemical, or alcohol foam to extinguish fires involving acrolein. Water may be ineffective, but it may be used to keep fire-exposed containers cool or to protect persons attempting to stop a leak involving this substance.

Fires involving acrolein should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of acrolein may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acrolein. Chemical protective clothing specifically recommended for acrolein may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acrolein.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrolein is 0.1 ppm (0.25 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 0.3 ppm (0.8 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.25 mg/m^3) as an 8-hr TWA and 0.3 ppm (0.8 mg/m^3) as a STEL [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acrolein a threshold limit value (TLV) of 0.1 ppm (0.23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (0.69 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of severe eye, nose, and respiratory irritation associated with exposure to acrolein.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to acrolein can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Acrolein is a severe irritant and corrosive to the eyes, skin, mucous membranes, and respiratory tract in animals. Eye contact with liquid acrolein has caused severe burns, corrosion, and corneal injury [Grant 1986; Proctor et al. 1988]. The dermal LD_{50} in rabbits is 562 mg/kg [NIOSH 1991]. Skin contact can cause erythema, edema, severe irritation, corrosion, and burns [NIOSH 1991]. The mouse RD_{50} (concentration that decreases respiratory rate by 50% in exposed animals) is 1.7 ppm [NLM 1992]. The 10-min, 30-min, and 8-hr LC_{50}s in rats are 375, 131, and 8 ppm, respectively [AIHA 1989]. Cats exposed for 3.5 hr to 10 ppm showed signs of respiratory irritation, mild narcosis, lacrimation, and salivation [ACGIH 1991a]. The oral LD_{50} is 42 to 46 mg/kg in rats and 28 mg/kg in mice [AIHA 1989]. When swallowed, acrolein induces gastrointestinal distress, pulmonary congestion, and edema [NLM 1992]. Rats, guinea pigs, dogs, and monkeys were repeatedly exposed to 0.7 or 3.7 ppm for 8 hr/day, 5 days/week for 6 weeks. All animals exposed to 0.7 ppm developed inflammatory lung changes. Emphysema was infrequently but more predominantly observed in dogs and monkeys than in rats or guinea pigs. Animals exposed to 3.7 ppm salivated and had ocular and respiratory irritation. Histopathology of survivors revealed nonspecific inflammatory changes in the lungs, liver, and kidneys. Squamous metaplasia of dog and monkey trachea and necrotizing bronchitis with squamous metaplasia of monkey lungs was also observed. In addition, these four species were continuously exposed to 0.21, 0.23, 1.0, or 1.8 ppm acrolein 24 hr/day for 90 days. Findings similar to those cited for the repeated exposure experiment were likewise observed, with the inflammatory changes also being noted in the brains of all acrolein-exposed animals [Lyon et al. 1970]. Male rats died (32 of 57) following exposures to 4 ppm for 6 hr/day, 5 days/week for 62 exposure days. Terminal histopathology revealed bronchiolar necrosis and pulmonary edema in treated animals [Proctor et al. 1988]. Intra-amniotic or intravenous administration of acrolein to pregnant rats induced malformations or embryolethality, respectively [NIOSH 1991]. Acrolein is mutagenic in bacterial test systems [NIOSH 1991]. Mice that were dermally injected with acrolein for 24 weeks did not develop injection-site sarcomas during the ensuing 70-week observation period [NLM 1992]. Syrian golden hamsters inhaled 4 ppm for 7 hr/day, 5 days/week for 52 weeks. Additional groups were also administered benzo(a)pyrene or

N-nitrosodiethylamine. Following 29 weeks without exposure, terminal sacrifice in week 81 demonstrated that no increased tumor incidence had been induced by acrolein [NLM 1992].

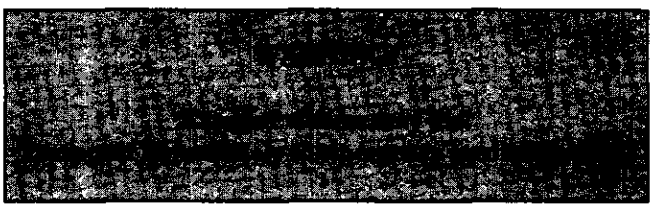
2. *Effects on Humans*: Acrolein is a powerful lacrimating agent and severe tissue irritant. Eye contact with liquid acrolein can cause pain, intense lacrimation, blepharoconjunctivitis, swelling of the lids, purulent discharge, photophobia, and corneal injury [Grant 1986; Gosselin et al. 1984; NLM 1992]. Contact of the skin with liquid acrolein causes redness, edema, swelling, vesiculation, and burns. In addition, acrolein can be absorbed through the skin in sufficient amounts to cause systemic effects [Gosselin et al. 1984]. This chemical is a weak skin sensitizer in some exposed individuals [Proctor et al. 1988]. Exposure to 0.25 ppm for 5 min causes moderate irritation of the eyes, mucous membranes, and upper respiratory tract [Clayton and Clayton 1981; Grant 1986]. Exposure to a 1-ppm (2.3-mg/m^3) concentration of acrolein vapor for the same interval is described as intolerable and causes intense lacrimation and severe eye, nose, and throat irritation [Clayton and Clayton 1981; Grant 1986]. Acrolein is a severe lung irritant and tear-inducer at 3 ppm (7 mg/m^3) [IARC 1985]. At higher exposure levels, it can induce significant delayed-onset lung injury, including dyspnea, asthma, congestion, edema, and persistent respiratory insufficiency with decreased pulmonary function [NLM 1992]. Prolonged exposure to 21 ppm causes pulmonary edema, and fatalities have been reported at concentrations as low as 10 ppm; exposure to 150 ppm for 10 min is lethal to humans [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acrolein can cause severe irritation or corrosion of the eyes, nose, throat, and lungs, with tearing, pain in the chest, and delayed-onset pulmonary injury with depressed pulmonary function. Contact of liquid acrolein with the eyes may cause corneal burns, corrosion, and blindness; skin contact may result in redness, swelling, chemical burns with blisters, and corrosion.

2. *Chronic exposure*: The signs and symptoms of chronic exposure to acrolein include skin sensitization and contact dermatitis.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of acrolein! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acrolein are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acrolein or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acrolein and may result in worker exposures to this substance:

—Use of acrolein as an intermediate in the production of glycerine and methionine analogs (poultry feed protein supplements)

—Manufacture of colloidal forms of metals, artificial resins, synthetic fibers, and polyurethane foams

—Chemical synthesis of 1,3,6-hexanetriol, glutaraldehydes, and acrylates

—Use of acrolein as a slimicide in the manufacture of paper

—Use of acrolein in biomedical applications to fix tissue and, with its polymers, to immobilize enzymes

—Subsurface injection of wastewaters to control the growth of microbes in feed lines and to control the growth of algae, aquatic weeds, and mollusks in recirculating process water systems

—Manufacture of pharmaceuticals, perfumes, and food supplements

—Use of acrolein as an alcohol denaturant

—Heating of oils and fats containing glycerol

—Use of acrolein as a liquid fuel

The following methods are effective in controlling worker exposures to acrolein, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to acrolein, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrolein at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and

other findings consistent with eye, skin, or respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acrolein exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acrolein on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acrolein.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acrolein is determined by using a solid sorbent sampling tube containing 2-(hydroxymethyl)piperidine on XAD-2 adsorbent. Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 48 liters is collected. The sample is then treated with toluene to extract the acrolein. Analysis is conducted by gas chromatography using a nitrogen-phosphorus detector. This method has a sampling and analytical error of 0.12 and is sufficiently sensitive for full-shift personal monitoring below the PEL of 0.1 ppm. For STEL measurements, the limit of the method is 0.8 ppm for a 15-min sample. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 52 of the *OSHA Analytical Methods Manual* [OSHA 1985]. A similar method (Method 2501) can be found in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If acrolein contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with acrolein should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of acrolein, particularly its potential to cause severe irritation of the eyes and skin.

A worker who handles acrolein should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acrolein or a solution containing acrolein is handled, processed, or stored.

STORAGE

Acrolein should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Acrolein must be stored under a nitrogen blanket. Uninhibited acrolein may not be stored, and the level of the inhibitor must be checked regularly during prolonged storage. The storage area should be equipped with an automatic sprinkler or other extinguishing system. All electrical service in the storage area must be of explosionproof design. Containers of acrolein should be protected from physical damage and should be stored separately from alkaline materials (such as caustics, ammonia, or amines), oxidizers, heat, sparks, and open flame. To prevent static sparks, containers and equipment should be grounded and bonded when transferring liquid acrolein. Because empty containers formerly containing acrolein may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acrolein, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Provide maximum explosionproof ventilation.

5. If feasible, remove leaking containers to a safe place.

6. Absorb small liquid spills with sand, vermiculite, or other noncombustible absorbent material and place the material in a covered container for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the acrolein for later reclamation or disposal, or absorb with vermiculite or sand.

8. After cleanup, the spill area should be washed thoroughly with soap and water.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

If 500 lb or more of acrolein is present at a facility, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for acrolein is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of acrolein per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acrolein emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acrolein is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. P003. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Acrolein also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acrolein exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that

involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with acrolein. Impervious clothing, gloves, boots, and other protective clothing are recommended when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The only material that has been tested against permeation by acrolein and has demonstrated good-to-excellent resistance for longer than 8 hr is butyl rubber. Natural rubber, neoprene, nitrile, polyvinyl alcohol, polyvinyl chloride, Teflon®, and Viton® have demonstrated poor resistance to permeation by acrolein.

If acrolein is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acrolein might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acrolein. Contact lenses should not be worn if the potential exists for acrolein exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLAMIDE

INTRODUCTION

This guideline summarizes pertinent information about acrylamide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_3H_5NO

- **Structure**

$H_2C=CHCONH_2$

- **Synonyms**

Acrylic amide; propenamide; 2-propenamide; propenoic acid amide; acrylamide monomer

- **Identifiers**

1. CAS No.: 79-06-1
2. RTECS No.: AS3325000
3. DOT UN: 2074 55
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

Acrylamide is a colorless to white, odorless, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 71.1
2. Boiling point (at 760 mm Hg): 175° to 300°C (347° to 572°F); decomposes on boiling
3. Specific gravity (water = 1): 1.1 at 30°C (86°F)
4. Vapor density (air = 1 at boiling point of acrylamide): 2.4
5. Melting point: 84.5°C (179.3°F)
6. Vapor pressure at 20°C (68°F): 0.007 mm Hg
7. Solubility: Miscible with water; soluble in acetone, ethanol, ethyl ether, and methanol
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Acrylamide decomposes above 175°C (347°F). Violent polymerization may occur when heated or when exposed to ultraviolet light.
2. Incompatibilities: Fires and explosions may result from contact of acrylamide with strong oxidizers.
3. Thermal decomposition products: Toxic gases (such as ammonia, hydrogen, and carbon monoxide) may be released when acrylamide decomposes; toxic oxides of nitrogen may form in fire.
4. Special precautions: None

- **Flammability**

Acrylamide is combustible, but because of its high flash point, it is considered only a slight fire hazard when exposed to heat, sparks, or open flame. It is a combustible, flammable liquid when dissolved in solvent. The National Fire Protection Association has not assigned a flammability rating to

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

acrylamide; other sources rate acrylamide as a moderate fire hazard.

1. Flash point: 138°C (280°F) (closed cup)

2. Autoignition temperature: 424°C (795°F)

3. Flammable limits in air (% by volume): Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam for small fires; water spray, fog, or standard foam for large fires.

Fires involving acrylamide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of acrylamide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool the containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acrylamide. Chemical protective clothing specifically recommended for acrylamide may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by acrylamide.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylamide is 0.03 mg/m^3 as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" designation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.03 mg/m^3 as an 8-hr TWA with a "Skin" notation. However, acrylamide has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated acrylamide an A2 substance (suspected human carcinogen) and assigned acrylamide a threshold limit value (TLV) of 0.03 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek with a "Skin" notation [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of systemic poisoning associated with exposure to acrylamide.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to acrylamide can occur through inhalation of vapor, dust, or aerosol and absorption through the skin or mucous membranes.

• Summary of toxicology

1. *Effects on Animals*: Acrylamide is an irritant, a potent neurotoxin that affects both the central and peripheral nervous systems, a reproductive toxin, and a carcinogen. A 10% aqueous solution of acrylamide applied to abraded rabbit skin caused tissue swelling and redness. Although the 10% aqueous solution immediately caused slight pain and conjunctival irritation, a 40% solution produced severe pain with minimal corneal damage. This damage was repaired within 24 hr following a nonrinsed ocular application [Grant 1986]. Acrylamide is also a moderate skin irritant. The acute dermal LD_{50} in rabbits is 2,250 mg/kg [ACGIH 1991a]. The acute oral LD_{50} for rats, guinea pigs, and rabbits fed aqueous solutions of 2.5% to 12.6% acrylamide ranged from 150 to 180 mg/kg body weight. However, in rats fed a 50% aqueous solution of acrylamide, the LD_{50} was 565 mg/kg and 490 mg/kg for males and females, respectively. The acute lethality of acrylamide is a result of its neurotoxic effects, especially on the central nervous system. The toxic effects of acrylamide on the central nervous system are reversible if the dose and duration of exposure are minimal. Recovery is greatly prolonged if the exposure duration is increased [ACGIH 1991a].

Severe or lethal exposure concentrations can also induce testicular degeneration of the seminephrous tubules, degeneration of the convoluted tubular epithelium of the kidney, fatty degeneration and necrosis of the liver, and congestion of the lungs [NLM 1991]. The primary effects of repeated exposures are neurotoxic and involve the central and peripheral nervous systems. The central nervous system effects predominate during acute and subchronic exposures and can also involve somnolence and hallucinations. The sensory and motor neuronal effects on the peripheral nervous system (such as distal numbness, paresthesias, sensory loss, weakness, ataxia, and paralysis) predominate during chronic exposures [NLM 1991]. Rats, cats, and monkeys have developed neuropathies only when exposed to repeated daily doses of 1 mg/kg or more [ACGIH 1991a].

Male rats and mice that received neurotoxic concentrations of acrylamide orally for 2 to 3 months developed testicular degeneration. The rats consumed 20 mg/kg of body weight per day from drinking water, which contained 400 ppm. The mice received doses of 35.5 mg/kg twice per week [NLM 1991]. Chromosomal alterations in the sperm (but not bone marrow) cells of male DDY mice exposed to acrylamide have also been reported [Sakamoto and Hashimoto 1986]. Although pregnant rats that consumed a diet containing 400 ppm throughout their gestation period developed maternal toxicity (neurotoxicity), only slightly depressed birth weights were noted in their pups [ACGIH 1991a]. Similar consumption of a 200-ppm diet induced an abnormal gait in the pregnant dams but did not affect the growth and development of offspring during their first 6 weeks of postnatal development [ACGIH 1991a]. No developmental defects were induced in fetuses of pregnant dams intubated with 20 mg/kg per day (200 mg/kg total dose) during days 6 to 17 of gestation [NLM 1991].

Studies in mice and rats confirm that acrylamide can act either as an initiator or as a complete carcinogen [NIOSH 1991]. This chemical induces skin-tumor-initiating activity in Sencar mice and lung tumors in A/J mice. Acrylamide administered in drinking water to F344 rats for 2 years caused a statistically increased number of tumors (including cancerous tumors) at multiple sites. The International Agency for Research on Cancer (IARC) found "sufficient evidence of carcinogenicity" for chronically exposed animals [IARC 1986].

2. *Effects on Humans*: Most cases of acrylamide toxicity in humans have resulted from occupational exposures, especially transcutaneous ones. In these cases, episodic contact dermatitis of the hands is usually observed before signs of severe neuropathy become apparent. Workers exposed through the skin to acrylamide dust for 1 to 24 months developed characteristic neurological signs that consisted of postural difficulty, ataxia, lethargy, loss of vibratory sensation, loss of deep tendon reflexes, loss of position sense, and weakness, numbness, and tingling of the extremities. In addition, the extremities were cold and bluish-red in color. The palms of the hands and soles of the feet sweated excessively, and skin peeled from the hands and fingers [Sax 1984; Schaumburg et al. 1983].

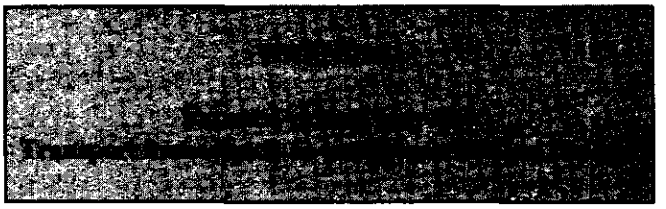
Acrylamide toxicity resulting from ingestion of subacute doses (such as in contaminated drinking water) is manifested by central nervous system neuropathy. Drowsiness, disturbed balance, confusion, memory loss, and hallucinations have all been reported following ingestion of acrylamide. Nystagmus and slurred speech have also been noted. Disturbances of vision have not been observed in cases of systemic acrylamide toxicity. In systemic acrylamide poisoning, peripheral neuropathy is late to appear relative to central nervous system effects. The signs and symptoms of acrylamide toxicity remit slowly, and often only partially, following cessation of exposure. Although IARC could find no adequate data that demonstrate an increased cancer incidence in acrylamide-exposed workers, they classify the chemical as 2B, "possibly carcinogenic to humans." This classification is based on the induction of cancers in exposed experimental animals [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Exposure to acrylamide can cause irritation, muscular stiffness and weakness, ataxia, loss of balance, loss of proprioception, and ability to stand.

2. *Chronic exposure*: Exposure to acrylamide can cause irritation, peeling of the skin and excessive sweating of the hands and feet, somnolence, confusion, hallucinations, memory loss, numbness, sensory loss, loss of tendon reflexes, weakness, nystagmus, slurred speech, incoordination, tremor, muscular atrophy, ataxia, and paralysis.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Acrylamide can cause skin irritation. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If respirable acrylamide is inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to swab particulates from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acrylamide is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of acrylamide may result in worker exposures to this substance:

—Use in the manufacture of copolymers and polyacrylamides for use as flocculating and thickening agents in pulp and paper industries, oil production, mining textiles, surface coating, adhesives, dyes, photography, and water and waste treatment

—Use as a grouting material in oil wells, basements, tunnels, mine shafts, caissons, and dams

—Use in miscellaneous processes of monomer acrylamide as a curing agent and in organic synthesis

—Use in soap and cosmetic preparations as thickeners and in preshave lotions, hair grooming preparations, and denture fixtures

—Use in stabilizing soil and in permitting the free flow of foundry sand into molds

—Use in clarifying solutions in chemical and food manufacturing; use in gel form in electrophoresis procedures in laboratories

The following methods are effective in controlling worker exposures to acrylamide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acrylamide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrylamide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical

condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history or findings consistent with seizure or other central nervous system disorders or chronic respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acrylamide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acrylamide on the central nervous system and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acrylamide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acrylamide is determined by using a personal sampling train consisting of a glass fiber filter in a Swinnex cassette (13 mm) followed by a silica gel tube. Plastic cassettes (37 mm) yielded poor recoveries of acrylamide and are therefore unsuitable. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 120 liters is collected. The silica gel tube should then be treated with methanol to extract the acrylamide. An important step in this method is the transfer of the glass-fiber filters to glass vials containing 1 ml of methanol immediately after sampling to avoid losses of acrylamide from the filter by evaporation. The sample is then analyzed by gas chromatography using a nitrogen/phosphorous detector. The limit of detection for this procedure is 1.3 parts per billion (ppb) (0.004 mg/m^3). This method (Method 21) is included in the OSHA Computerized Information System [OSHA 1986]. The NIOSH procedure (Method S158) is described in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Because acrylamide can be absorbed through the skin in lethal amounts, workers should immediately remove any contaminated clothing and then should wash thoroughly with soap and water any areas of the skin that have come in contact with this substance.

Clothing and shoes contaminated with acrylamide should be removed immediately and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of acrylamide, particularly its potential for being absorbed through the skin in lethal amounts.

A worker who handles acrylamide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acrylamide is handled, processed, or stored.

STORAGE

Acrylamide should be stored in a dark, dry, well-ventilated refrigerated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage in an inert atmosphere is recommended. All electrical service in storage areas should be of explosionproof design. Containers of acrylamide should be protected from physical damage and should be stored separately from oxidizing agents, polymerization catalysts, heat, sparks, and open flame. Because empty containers may contain acrylamide residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acrylamide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Provide maximum explosionproof ventilation.

5. Use nonsparking tools during cleanup.

6. Carefully collect solid material using sand, vermiculite, or soda ash and place in a covered container for disposal.

7. To the extent feasible, avoid generating dust during cleanup.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acrylamide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of acrylamide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acrylamide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although acrylamide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acrylamide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with acrylamide. Gloves, apron, boots, and a chemical protective suit should be worn when workers are handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Polyethylene/ethylene vinyl alcohol has been tested against permeation by acrylamide and has demonstrated good-to-excellent resistance for periods of 4 to 8 hr.

If acrylamide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acrylamide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acrylamide. Contact lenses should not be worn if the potential exists for acrylamide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLIC ACID

INTRODUCTION

This guideline summarizes pertinent information about acrylic acid for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_3H_4O_2$

- **Structure**

$CH_2{=}CHCO_2H$

- **Synonyms**

Propenoic acid, acroleic acid, ethylenecarboxylic acid, propene acid, vinylformic acid, glacial acrylic acid, 2-propenoic acid

- **Identifiers**

1. CAS No.: 79-10-7
2. RTECS No.: AS4375000
3. DOT UN: 2218 29
4. DOT label: Corrosive

- **Appearance and odor**

Acrylic acid is a colorless, corrosive, combustible liquid with a distinctive and acrid odor. The odor threshold is reported to be 1.0 part per million (ppm) parts of air. Acrylic acid is available commercially in the United States in two forms: the technical grade (which contains 94% acrylic acid) and glacial acrylic acid (which contains 98% acrylic acid).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 72.1
2. Boiling point (760 mm Hg): 141°C (221.8°F)
3. Specific gravity (water = 1): 1.06 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of acrylic acid): 2.5
5. Melting point: 14°C (57.2°F)
6. Vapor pressure at 20°C (68°F): 3.1 mm Hg
7. Solubility: Miscible with water, alcohol, ether, acetone, and benzene
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: The vapor forms an explosive mixture in contact with the air. Heat, sparks, open flame, oxygen, high temperature, and pressure.
2. Incompatibilities: Fires and explosion may result from contact of acrylic acid with oxydizing agents, amines, alkalis, ammonium hydroxide, chlorosulfonic acid, ethylene diamine, ethyleneimine, oleum, or 2-aminoethanol.
3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released in a fire involving acrylic acid.
4. Special precautions: Acrylic acid corrodes carbon steel and other metals.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to acrylic acid.

1. Flash point: 50°C (122°F) (open cup)
2. Autoignition temperature: 438°C (820°F)
3. Flammable limits in air (% by volume): Lower, 2.4; upper, 8.0
4. *Extinguishant:* Use dry chemical, water spray, alcohol foam, or carbon dioxide to fight fires involving acrylic acid.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving acrylic acid should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of acrylic acid may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acrylic acid. Firefighters' protective clothing may not provide protection against permeation by acrylic acid.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylic acid is 10 ppm (30 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (6 mg/m^3) as an 8-hr TWA with a "Skin" notation [NIOSH 1988, 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acrylic acid a threshold limit value (TLV) of 2 ppm (5.9 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991]. The ACGIH TLV also bears a "Skin" notation.

• Rationale for limits

The OSHA limit was established to protect workers from the risk of eye and nasal irritation. The NIOSH and ACGIH limits were based on recent studies demonstrating degeneration of nasal mucosa at 5 ppm, changes in pulmonary function, teratogenicity and embryotoxicity in rats at low doses, and skin absorption in animals.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to acrylic acid can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

• Summary of toxicology

1. *Effects on Animals*: Acrylic acid is dermally absorbed and is corrosive to the eyes, nose, and mucous membranes in animals. Application of glacial acrylic acid to the eyes of rabbits caused irreversible corneal injury graded 9 on an ascending severity scale of 1 to 10 [Grant 1986]. Application of a 1% solution to the eye of a rabbit caused severe burns and eye injury [ACGIH 1991a; NIOSH 1991; Proctor et al. 1988]. Irreversible eye and skin damage resulted following exposure of rats to 1,200 ppm for 4 hr [NLM 1992]. Applied to rabbit skin, acrylic acid caused severe irritation [Proctor et al. 1988]. Three of five guinea pigs became dermally sensitized when exposed to acrylic acid by injection and subsequently challenged with this substance [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is 290 mg/kg [NLM 1992]. Saturated atmospheres have been reported to range from 420 ppm at 20° to 760 ppm at 30° [NLM 1992]. Although exposure of rats to polymerized saturated vapors (room temperature) for 8 hr did not induce deaths [Smyth et al. 1962], a 1-hr exposure to unpolymerized saturated vapor was the maximum duration tolerated without death [Carpenter et al. 1974]. Vapor concentrations approaching saturation killed half of a group of rats exposed for 3.5 hr [NLM 1992]. However, 4-hr exposures of rats at 2,000 or 4,000 ppm were nonlethal [NLM 1992; Carpenter et al. 1974]. The 4-hr LC_{50} in rats is 1,200 ppm [NLM 1992]. Exposure of rats to irritant concentrations of acrylic acid caused decreased respiratory rates and tidal and minute volumes [ACGIH 1991a]. In addition, four rats exposed once to 6,333 ppm of acrylic acid for 5 hr developed eye and nose irritation, respiratory difficulties, and unresponsivness; one animal died. At autopsy, these animals showed lung, liver, and kidney damage [ACGIH 1991a]. The oral LD_{50} in rats was variable: 357, 1,250, or 2,722 mg/kg [NLM 1992; Smyth et al. 1962]. Rats exposed to acrylic acid at 80 ppm for 6 hr/day, 5 days/week for 4 weeks showed no adverse effects, and rats exposed to 300 ppm on the same regimen experienced nose irritation, lethargy, and decreased weight

gain. Rats exposed to 1,500 ppm acrylic acid for shorter intervals showed damage to the liver, kidneys, and lungs at autopsy [ACGIH 1991a]. However, rats that inhaled 233 ppm for 4 hr/day, 5 days/week for 4 weeks developed gastric mucosal lesions and pulmonary inflammation [NLM 1992]. In rats exposed to the vapors of acrylic acid at 5, 25, or 75 ppm for 6 hr/day, 5 days/week for 13 weeks, terminal pathology was normal in the 5- or 25-ppm group; however, slight degenerative lesions of the olfactory mucosa were present in the high-dose group [ACGIH 1991a]. Similarly exposed mice were more sensitive than rats as they developed lesions of the nasal mucosa for all three exposure concentrations [ACGIH 1991a]. Intraperitoneal or intra-amniotic injections of acrylic acid caused embryotoxicity and gross abnormalities in the offspring of treated pregnant rats [Proctor et al. 1988; NLM 1992].

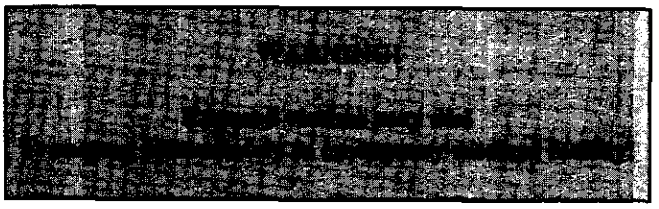
2. *Effects on Humans*: Acrylic acid is corrosive on contact with the eyes, skin, mucous membranes, and upper respiratory tract of humans, and its vapor causes severe irritation of these organs. Acute industrial exposure to this substance has caused eye and skin burns ranging in intensity from moderate to severe [Proctor et al. 1988]. Absorption of acrylic acid through the skin has been reported to cause systemic illness, and inhalation of the mist or vapor of acrylic acid may cause lung injury as well as nasal irritation and tearing of the eyes [Genium 1989]. Based on effects seen in animals, acrylic acid may cause skin sensitization [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to acrylic acid can cause redness, swelling, and tearing of the eyes, runny nose, scratchy throat, coughing, and difficult breathing. Contact of the liquid with the eyes or skin can cause corneal injury, irritation, burns, and destruction of the tissue.

2. *Chronic exposure*: Chronic exposure to acrylic acid may cause lethargy, irritation, and skin sensitization reactions.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of acrylic acid. ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of acrylic acid are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if acrylic acid or a solution containing it is ingested:

—Seek medical attention ***immediately***.

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acrylic acid and may result in worker exposures to this substance:

—Manufacture of acrylic resins, especially the acrylates

—Use of acrylic acid in acrylic polymeric emulsions for leather, textile, and paper coatings

—Use of acrylic acid in paints, floor polishes, adhesives, general finishes, and binders

—Manufacture of plastics, molding powder for signs, construction units, decorative emblems, and insignia

—Use of acrylic acid in dentistry and medicine

The following methods are effective in controlling worker exposures to acrylic acid, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acrylic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrylic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acrylic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying

the adverse effects of acrylic acid on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acrylic acid.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne acrylic acid is determined by using two XAD-8 tubes connected in series. Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 24 liters is collected. The sample is then treated with methanol and water (1:1) to extract the acrylic acid. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method has a sampling and analytical error of 0.12 and is found in OSHA Method No. 28, *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

If acrylic acid contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, followed by washing with soap and water.

Clothing contaminated with acrylic acid should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of acrylic acid, particularly its potential to cause skin burns.

A worker who handles acrylic acid should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acrylic acid or a solution containing acrylic acid is handled, processed, or stored.

STORAGE

Acrylic acid is explosive unless (1) an inhibitor has been added to it before it is stored, or (2) it is stored at temperatures below its melting point. Acrylic acid should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; the storage area must meet the requirements for an OSHA Class II combustible liquid. Explosionproof exhaust ventilation and sparkproof fans must be used in storage areas. Storage tanks should be made of stainless steel or aluminum. Containers of acrylic acid should be protected from physical damage and should be stored separately from oxidizers, amines, alkalies, other incompatible substances, heat, sparks, and open flame. Only nonsparking tools may be used to handle acrylic acid. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained acrylic acid may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving acrylic acid, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Use water spray to reduce vapors, but the spray may not prevent ignition in closed spaces.

6. Use nonsparking tools for cleanup.

7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the acrylic acid for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Acrylic acid is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by EPA regulation resulting from the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for acrylic acid is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of acrylic acid per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acrylic acid emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Acrylic acid is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U008. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Acrylic acid may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acrylic acid exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an

evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any possibility of skin contact with acrylic acid. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by acrylic acid and have demonstrated good-to-excellent resistance for periods greater than 8 hr: butyl rubber and Saranex®. Materials that may withstand permeation for more than 4 hr but fewer than 8 hr: Teflon® and Viton®. Natural rubber, neoprene, nitrile rubber, polyethylene, and polyvinyl chloride have demonstrated poor resistance to permeation by acrylic acid.

If acrylic acid is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acrylic acid might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acrylic acid. Contact lenses should not be worn if the potential exists for acrylic acid exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLONITRILE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about acrylonitrile for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_3H_3N
- **Structure:**

$$CH_2=\underset{\displaystyle CN}{CH}$$

- **Synonyms:** Acrylon, AN, carbacryl, cyanoethylene, fumigrain, propenenitrile, VCN, ventox, vinyl cyanide
- **Identifiers:** CAS 107-31-1; RTECS AT5250000; DOT 1093, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Pale yellow liquid with an unpleasant odor similar to pyridine

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 53.07
2. Boiling point (at 760 mmHg): 77.3°C (171°F)
3. Specific gravity at 20°C (68°C) (water = 1): 0.81
4. Vapor density (air = 1 at boiling point of acrylonitrile): 1.83
5. Melting point: -83°C (-117°F)
6. Vapor pressure at 20°C (68°F): 83 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 7.35
8. Evaporation rate (butyl acetate = 1): 4.54
9. Saturation concentration in air (approximate) at 20°C (68°F): 10.9% (109,000 ppm)
10. Ionization potential: 10.91 eV

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers, especially bromine, and strong bases may cause fires and explosions. Contact with copper, copper alloys, ammonia, or amines may cause decomposition. Acrylonitrile will polymerize when hot, and the additional heat liberated by the polymerization may generate high internal pressure and cause containers to explode. Inhibitors are added to the commercial product to prevent self-polymerization.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving acrylonitrile.
3. Caution: Acrylonitrile will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -1°C (30°F) (closed cup)
2. Autoignition temperature: 481°C (898°F)
3. Flammable limits in air, % by volume: Lower, 3; Upper, 17
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: Approximately 20 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylonitrile is 2 parts of acrylonitrile per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the OSHA ceiling concentration which shall at no time be exceeded is 10 ppm as determined in any 15-minute sampling period (Skin). The notation for "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that acrylonitrile be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 1 ppm as a TWA for up to an 8-hour workshift, 40-hour workweek; the NIOSH ceiling concentration is 10 ppm as determined in any 15-minute sampling period (Skin). The American Conference of Governmental In-

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dustrial Hygienists (ACGIH) has designated acrylonitrile as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 2 ppm [4.5 milligrams of acrylonitrile per cubic meter of air (4.5 mg/m³)] as a TWA for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational Exposure Limits for acrylonitrile

	Exposure limits ppm	mg/m³
OSHA PEL TWA (Skin)*	2	—
Ceiling (15 min) (Skin)	10	—
NIOSH REL TWA (Skin) (Ca)†	1	—
Ceiling (15 min) (Skin)	10	—
ACGIH TLV® TWA (Skin) (A2)§	2	4.5

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure
Acrylonitrile may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology
1. *Effects on animals:* In rats, guinea pigs, or dogs, acute inhalation or oral administration of acrylonitrile caused signs of toxicity including decreased water and food consumption, decreased weight gain, histologic changes in the brain resembling anoxia, or damage to the lungs, liver, or kidneys. In rats, chronic inhalation or oral administration of acrylonitrile produced tumors of the brain, stomach, ear canal, and mammary glands, and cancer of the Zymbal gland. Oral administration of acrylonitrile to pregnant rats caused embryotoxic and teratogenic effects.
2. *Effects on humans:* Two separate studies of workers who were potentially exposed to acrylonitrile and who were observed over an 18- or 20-year period showed increased incidences of lung and colon cancers. In addition, at least two deaths from accidental inhalation or skin absorption of acrylonitrile have occurred.

• Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to acrylonitrile can cause eye irritation, headache, sneezing, nausea, vomiting, weakness, light-headedness, and asphyxia.
2. *Long-term (chronic):* Skin contact with acrylonitrile can cause burns, blisters, and dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation
Prior to placing a worker in a job with a potential for exposure to acrylonitrile, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, gastrointestinal tract, and respiratory, reproductive, and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to acrylonitrile at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis, and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to acrylonitrile. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, gastrointestinal tract, and respiratory, reproductive, and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination.**
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to acrylonitrile may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**
Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**
Measurements to determine worker exposure to acrylonitrile should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Ceiling concentration evaluation**
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of acrylonitrile. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**
Sampling and analysis may be performed by collecting acrylonitrile vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure acrylonitrile may also be used if available. A detailed sampling and analytical method for acrylonitrile may be found in the *NIOSH Manual of Analytical Methods* (method number 1604).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with acrylonitrile.

SANITATION

Clothing which is contaminated with acrylonitrile should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of acrylonitrile from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of acrylonitrile's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with acrylonitrile should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle acrylonitrile should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to acrylonitrile may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for acrylonitrile

Operations	Controls
During use in the manufacture of ABS resin, SAN resin, plastic, or surface coating materials	Total enclosure
During the manufacture and transfer of monomer to other reaction vessels or to tank cars.	Total enclosure, local exhaust ventilation, personal protective equipment
During use as a chemical intermediate; during use in the cyanoethylation of cotton	Local exhaust ventilation, personal protective equipment
During use in surface coating applications	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to acrylonitrile, an eye-wash fountain should be provided within the immediate work area for emergency use.

If acrylonitrile gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to acrylonitrile, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If acrylonitrile gets on the skin, wash it immediately with soap and water. If acrylonitrile penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If acrylonitrile is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing acrylonitrile, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing acrylonitrile may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing acrylonitrile may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for acrylonitrile

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALDRIN

POTENTIAL HUMAN CARCINOGEN

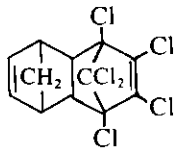
INTRODUCTION

This guideline summarizes pertinent information about aldrin for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

NOTE: Most uses of aldrin were suspended by the U.S. Environmental Protection Agency, effective October 18, 1974. The only uses allowed are direct soil application, seed treatment if labeled "not for food use," dipping of plant roots and tops, subsurface termite control, and hot-caps.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{12}H_8Cl_6$
- **Structure:**



- **Synonyms:** Aldrex; aldrine; aldrosol; octalene; 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1,4-endo-5,8-dimethanonaphthalene
- **Identifiers:** CAS 309-00-2; RTECS 102100000; DOT 2761, label required: "Poison"
- **Appearance and odor:** Light to dark brown crystals with a mild chemical odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 364.90
2. Boiling point (at 760 mmHg): Decomposes
3. Specific gravity (water = 1): 1.6
4. Melting point: 104°C (219°F)
5. Vapor pressure at 20°C (68°F): 6.0 x 10^{-6} mmHg
6. Solubility in water: 0.027 mg/l at 27°C (80.6°F)

- **Reactivity**

1. Incompatibilities: Aldrin may react with concentrated mineral acids, acid catalysts, acid oxidizing agents, phenols, or reactive metals.
2. Hazardous decomposition products: Hydrochloric acid fumes and other chlorinated decomposition products may be released in a fire involving aldrin.
3. Caution: Aldrin should be stored in tightly closed containers in a well-ventilated area.

- **Flammability**

Aldrin is nonflammable.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for aldrin is 0.25 milligrams of aldrin per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that aldrin be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.15 mg/m³ as a TWA for up to a 10-hour workshift, 40-hour workweek. The NIOSH REL is the lowest concentration detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.25 mg/m³ (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

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Table 1.—Occupational exposure limits for aldrin

	Exposure limits mg/m³
OSHA PEL TWA (Skin)*	0.25
NIOSH REL TWA (Ca)†	§0.15
ACGIH TLV® TWA (Skin)	0.25

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ Lowest reliably detectable level.

HEALTH HAZARD INFORMATION

• **Routes of exposure**
Aldrin may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact. Dermal absorption is substantially increased when aldrin is dissolved in organic solvents.

• **Summary of toxicology**
1. *Effects on animals:* Acute or chronic oral administration of aldrin to dogs and rats produced liver and kidney degeneration; chronic oral administration produced liver cancer in mice and thyroid cancer in rats. Aldrin fed to pregnant hamsters and mice caused increased fetal deaths, as well as congenital anomalies and growth retardation in the offspring.
2. *Effects on humans:* Aldrin is a neurotoxin and has caused electroencephalogram abnormalities following short-term or long-term oral, dermal, or inhalation exposure.

• **Signs and symptoms of exposure**
1. *Short-term (acute):* Exposure to aldrin can cause hyperirritability, headache, dizziness, nausea, vomiting, blood in the urine, tremors, convulsions, and coma.
2. *Long-term (chronic):* Exposure to aldrin can cause redness of the skin and dermatitis, weight loss, muscular twitching, and convulsions.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**
Prior to placing a worker in a job with a potential for exposure to aldrin, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, endocrine glands, and hematopoietic (blood-cell-forming), reproductive, and nervous systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to aldrin at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include: preexisting chronic diseases of the skin, liver, kidneys, endocrine glands, and hematopoietic, reproductive, and nervous systems. Workers should inform their physicians of their potential for exposures to aldrin because internal absorption of this chemical pathologically increases the liver's ability to metabolize and eliminate medications which may be prescribed or taken "over the counter." The physician should obtain baseline values for liver function tests and a complete blood count with reticulocyte count.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to aldrin. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, eyes, liver, kidney, and hematopoietic, reproductive, and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to aldrin may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include: Non-autoimmune hemolytic anemia.
2. Delayed-onset SHE's include: Cataract, toxic hepatitis, and non-autoimmune hemolytic anemia.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to aldrin should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting aldrin with a glass-fiber filter and a midget impinger containing isooctane. The filter is extracted using isooctane, and analysis is performed using a gas chromatograph with an electrolytic conductivity detector. A detailed sampling and analytical method for aldrin may be found in the *NIOSH Manual of Analytical Methods* (method number 5502).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with aldrin.

SANITATION

Clothing which is contaminated with aldrin should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of aldrin from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of aldrin's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with aldrin should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle aldrin should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to aldrin may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for aldrin

Operations	Controls
During formulation and handling of insecticide	Personal protective equipment, local exhaust ventilation
During maintenance of equipment and storage containers	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to aldrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

If aldrin gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to aldrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If aldrin gets on the skin, wash it immediately with soap and water. If aldrin penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If aldrin is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Aldrin solid may be collected and placed in an appropriate container.
3. Aldrin solid or liquid may be collected by vacuuming with an appropriate high-efficiency filtration system.
4. For small quantities of liquids containing aldrin, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing aldrin may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for aldrin

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALLYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about allyl alcohol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_3H_6O

- **Structure**

$CH_2=CHCH_2OH$

- **Synonyms**

3-Hydroxypropene, 1-propene-3-ol, propenol, 2-propenol, 2-propenyl alcohol, allylic alcohol, 2-propene-1-ol, vinyl carbinol, Weed Drench

- **Identifiers**

1. CAS No.: 107-18-6
2. RTECS No.: BA5075000
3. DOT UN: 1098 57
4. DOT labels: Flammable Liquid, Poison

- **Appearance and odor**

Allyl alcohol is a clear, colorless, flammable liquid with a pungent, mustardlike odor. The odor threshold is reported to be below 0.8 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 58.1
2. Boiling point (at 760 mm Hg): 96°C (205°F)
3. Specific gravity (water = 1): 0.85 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of allyl alcohol): 2.0
5. Melting point: −129°C (−200.2°F)
6. Vapor pressure at 20°C (68°F): 19 mm Hg
7. Solubility: Miscible with water, alcohol, chloroform, ether, and petroleum ether
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame
2. Incompatibilities: Fire and explosion may result from contact of allyl alcohol with carbon tetrachloride, chlorosulfonic acid, diallyl phosphite plus phosphorus trichloride, nitric acid, oleum, sodium hydroxide, sulfuric acid, tri-n-bromomelamine, metal halides, caustic soda, or sodium, potassium, magnesium, aluminum, or their alloys.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be produced when allyl alcohol decomposes.
4. Special precautions: Allyl alcohol attacks some coatings and forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to allyl alcohol.

1. Flash point: 21.1°C (70°F) (closed cup)
2. Autoignition temperature: 378.3°C (713°F)

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1992

3. Flammable limits in air (% by volume): Lower, 2.5; upper, 18.0

4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving allyl alcohol. Water may be ineffective, but it may be used to keep fire-exposed containers cool. If a leak or a spill has not ignited, water spray should be used to disperse the vapors and protect the individuals attempting to stop the leak.

Fires involving allyl alcohol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of allyl alcohol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving allyl alcohol. Chemical protective clothing that is specifically recommended for allyl alcohol may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by allyl alcohol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for allyl alcohol is 2 ppm (5 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 4 ppm (10 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (5 mg/m^3) as an 8-hr TWA and 4 ppm (10 mg/m^3) as a STEL with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned allyl alcohol a threshold limit value (TLV) of 2 ppm (4.8 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek with a "Skin" notation and a STEL of 4 ppm (9.5 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of systemic effects and irritation associated with exposure to allyl alcohol.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to allyl alcohol can occur through inhalation, ingestion, or contact with the skin, eyes, or mucous membranes. Allyl alcohol is rapidly absorbed through the skin.

• Summary of toxicology

1. *Effects on Animals*: Allyl alcohol is a severe irritant of the eyes, nose, upper respiratory tract, and skin in animals; it also causes neurotoxic effects by all routes of exposure [Clayton and Clayton 1981]. Contact of this substance with the eyes of rabbits caused transitory corneal opacity, and skin contact caused mild irritation [NIOSH 1991; Grant 1986]. Although the 4- and 8-hr LC_{50}s in rats are 165 and 76 ppm, respectively, the lowest 4-hr lethal concentration in monkeys is 1,000 ppm [NIOSH 1991]. Rats acutely exposed to 3.9 ppm (a concentration capable of depressing the respiration rate by 50%) exhibited no signs of pulmonary irritation at necropsy [NLM 1991]. Animals sacrificed following acute inhalation showed signs of pulmonary edema and liver congestion and damage at autopsy [Proctor et al. 1988]. When rats were administered allyl alcohol and allowed 96 hr to recover before sacrifice, they developed acidophilia, vacuolation, and necrosis of the pancreatic acinar cells [NLM 1991]. The lowest reported oral LD_{50} in rats is 64 mg/kg [NIOSH 1991]. The dermal LD_{50} in rabbits is 45 mg/kg [NIOSH 1991]. Rats, rabbits, guinea pigs, and dogs exposed to 7 ppm for 7 hr/day during a 6-month period developed cloudy swelling and focal necrosis of the liver plus necrosis of the renal convoluted tubules. These effects were mild and reversible when exposure was discontinued [NLM 1991]. Rats that consumed drinking water containing allyl alcohol (100, 200, or 800 ppm for 15 weeks) had a dose-related decrease in water intake, food consumption, and weight gain but an increase in terminal organ weights for the liver, spleen, and kidneys [NLM 1991]. Allyl alcohol is directly mutagenic in some bacterial test systems [NIOSH 1991; NLM 1991].

2. *Effects on Humans*: Allyl alcohol is a severe irritant of the eyes, nose, upper respiratory tract, and skin in humans;

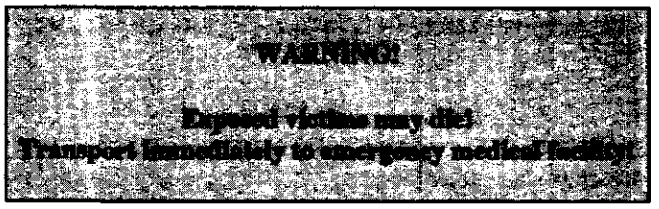
this substance can be absorbed through the skin in sufficient amounts to cause systemic toxicity. One man was temporarily blinded after being exposed to the vapor of allyl alcohol [Clayton and Clayton 1981]. Irritation of the eyes with tearing is noticeable at 5 ppm in some individuals, and irritation of the nose and throat begins at 10 to 15 ppm [ACGIH 1991a; Grant 1986]. Allyl alcohol is well absorbed through the skin, producing deep muscle pain believed to be caused by muscle spasm [Clayton and Clayton 1981]. In contact with the skin, allyl alcohol causes chemical burns with vesiculation and superficial necrosis [NLM 1991]. Inhalation exposures may lead to pulmonary edema [NLM 1991]. One worker died following a 1-hr exposure to 1,000 ppm [NIOSH 1991]. Systemic toxicity is manifested in humans as visceral congestion, periportal congestion of the liver, nephritis, and blood in the urine [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to allyl alcohol can cause irritation of the nose, throat, and lungs, and severe overexposure may lead to pulmonary edema with slowly developing distress. Burns and corrosion of the skin plus muscle pain can occur following prolonged contact with the liquid. Exposure of the eyes to liquid or vapor causes irritation, tearing, pain behind the eyeballs, transient corneal injury, and blurred vision and photophobia during exposure to light.

2. *Chronic exposure*: No signs or symptoms of chronic allyl alcohol exposure have been reported, but it may exacerbate chronic respiratory, liver, and kidney disease.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of allyl alcohol. ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of allyl alcohol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if allyl alcohol or a solution containing it is ingested:

—Seek medical attention ***immediately***.

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve allyl alcohol and may result in worker exposures to this substance:

—Preparation of various allyl esters that serve as monomers and prepolymers in the manufacture of resins and plasticizers

—Use of allyl alcohol as a chemical intermediate

—Manufacture of pharmaceuticals and military poison gas

—Use of allyl alcohol as a fungicide, herbicide, and nematicide

—Manufacture of flavorings, perfumes, allyl esters, glycerol, acrolein, and glycerin

The following methods are effective in controlling worker exposures to allyl alcohol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to allyl alcohol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, respiratory tract, kidney, and liver. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to allyl alcohol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, respiratory, kidney, or liver disease.

• Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to allyl alcohol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of allyl alcohol on the eyes, skin, respiratory system, kidneys, and liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although alcohols can be detected in the blood and urine of exposed individuals, no biological monitoring test acceptable for routine use has yet been developed for allyl alcohol.

• Medical examinations recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termina-

tion. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne allyl alcohol is determined by using a solid sorbent tube (100/50-mg sections, 20/40 mesh) filled with coconut shell charcoal. Samples are collected at a maximum flow rate of 0.2 liter/min until a minimum air volume of 10 liters is collected. The sample is then treated with a carbon disulfide/dimethylformamide solution to extract the allyl alcohol. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.18. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 1402 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Because allyl alcohol can be absorbed through the skin in lethal amounts, workers should immediately and thoroughly wash with soap and water any areas of the skin that have come in contact with this substance.

Clothing and shoes contaminated with allyl alcohol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of allyl alcohol, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles allyl alcohol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where allyl alcohol or a solution containing allyl alcohol is handled, processed, or stored.

STORAGE

Allyl alcohol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room that is separated from all oxidizing agents. Storage facilities and electrical service should be appropriate for this OSHA Class IB flammable liquid [29 CFR 1910.106]. Containers of allyl alcohol should be protected from physical damage and should be stored separately from oxidizing agents, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded when this substance is transferred from one container to another. Only nonsparking tools may be used to handle allyl alcohol. Because empty containers that formerly contained allyl alcohol may contain product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving allyl alcohol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors if the spill or leak has not ignited.
6. Absorb small spills with vermiculite, sand, or other noncombustible materials and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the allyl alcohol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

If 1,000 lb or more of allyl alcohol is present at a facility, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the

reportable quantity for that chemical, employers are required by EPA regulation resulting from the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for allyl alcohol is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

• Community right-to-know requirements

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of allyl alcohol emitted or released from their facility annually.

• Hazardous waste management requirements

EPA considers waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Allyl alcohol is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. P005. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Allyl alcohol may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of allyl alcohol are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

• Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous substances to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of allyl alcohol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

• Respiratory protection program

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Because allyl alcohol can be absorbed through the skin in lethal amounts, protective clothing should be worn to prevent skin contact. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by allyl alcohol and have demonstrated good-to-excellent resistance: butyl rubber, Viton®, and Teflon®. Both butyl rubber and Teflon may provide more than 8 hr of resistance to permeation by allyl alcohol. Neoprene, natural rubber, and polyvinyl alcohol have demonstrated poor resistance to permeation by allyl alcohol.

Safety glasses, goggles, or face shields should be worn during operations in which allyl alcohol might contact the

eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with allyl alcohol. Contact lenses should not be worn if the potential exists for allyl alcohol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALLYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about allyl chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_3H_5Cl

- **Structure**

$CH_2{=}CHCH_2Cl$

- **Synonyms**

3-Chloropropene, 1-chloro-2-propene, α-chloropropylene, chlorallylene, 3-chloropene, 3-chloro-1-propene, 3-chloropropylene, 2-propenyl chloride

- **Identifiers**

1. CAS No.: 107-05-1
2. RTECS No.: UC7350000
3. DOT UN: 1100 57
4. DOT labels: Flammable Liquid, Poison

- **Appearance and odor**

Allyl chloride is a colorless, yellow, or purple liquid with an unpleasant, garliclike odor. The odor threshold is reported to be 0.47 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76.5
2. Boiling point (at 760 mm Hg): 44° to 45°C (111.2° to 113°F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of allyl chloride): 2.6
5. Melting point: -134.5°C (-209°F)
6. Vapor pressure at 20°C (68°F): 295 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, chloroform, ether, and petroleum ether
8. Evaporation rate (butyl acetate = 1): Approximately 7

- **Reactivity**

1. Conditions contributing to instability: Violent polymerization and explosions may occur when allyl chloride is heated or comes into contact with acid catalysts, ferric chloride, aluminum chloride, Lewis acids, or Ziegler-type initiators.
2. Incompatibilities: Fires and explosions may result from contact of allyl chloride with ethylene diamine, ethyleneimine, oleum, chlorosulfonic acid, or with benzene or toluene in the presence of ethyl aluminum dichloride or ethyl aluminum sesquichloride.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving allyl chloride.
4. Special precautions: Allyl chloride attacks some coatings and some forms of plastic and rubber. This substance is also highly corrosive to steel.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to allyl chloride.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Flash point: -31.7°C (-25°F) (closed cup)

2. Autoignition temperature: 391°C (737°F)

3. Flammable limits in air (% by volume): Lower, 3.3; upper, 11.1

4. Extinguishant: Use carbon dioxide, dry chemical, or alcohol foam to extinguish fires involving allyl chloride; do *not* use a solid stream of water because the stream will scatter and spread the fire.

Fires involving allyl chloride should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of allyl chloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a cylinder becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving allyl chloride. Chemical protective clothing that is specifically recommended for allyl chloride may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by allyl chloride.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for allyl chloride is 1 ppm (3 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 2 ppm (6 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (3 mg/m^3) as a TWA for an 8-hr workshift and a 40-hr workweek and 2 ppm (6 mg/m^3) as a STEL [NIOSH 1988].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned allyl chloride a threshold limit value (TLV) of 1 ppm (3 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 2 ppm (6 mg/m^3) for periods not to exceed 15 min. The TLV also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overexposure [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of liver and kidney damage, and neuropathic effects associated with exposure to allyl chloride. The TLV also recommends a "Skin" notation; however, the TLV Committee has solicited quantitative data to serve as a basis for further evaluating the need for a "Skin" notation [ACGIH 1991a].

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to allyl chloride can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Allyl chloride is an irritant of the eyes, mucous membranes, and skin in animals; chronic exposure causes liver, kidney, lung, and nervous system damage. When instilled into the eyes of rabbits, allyl chloride caused damage rated as 2 on an ascending severity scale of 1 to 10 [Grant 1986]. Prolonged contact of allyl chloride with the skin causes moderate irritation [Clayton and Clayton 1981; NIOSH 1991]. The maximum acute allyl chloride exposures survived by rats were 29,300 ppm for 15 min, 2,900 ppm for 1 hr, and 290 ppm for 3 hr [NLM 1992]. Mice and rats have also survived 6-hr acute exposures of 800 ppm but not 1,000 to 2,000 ppm. The no-effect level in rats was 200 ppm, and dose-related kidney damage was induced in mice and rats exposed to ≥500 and 300, respectively [ACGIH 1991a]. One of six rats died following an acute 4-hr exposure of 2,000 ppm [Smyth and Carpenter 1948]. The 2-hr LC_{50} was 3,514 ppm in rats and 3,674 ppm in mice. The target organs of toxicity were the liver, kidneys, nervous system, and lungs [ACGIH 1991a]. Rats exposed to 16,000 ppm for 2 hr developed eye and nose irritation, weakness, incoordination, drowsiness, and dyspnea before death. Histopathology at autopsy revealed pulmonary hemorrhage, severe kidney damage, and mild liver injury [Proctor et al. 1988]. Tissue burns and pulmonary edema may develop on a delayed basis [NLM 1992]. The dermal LD_{50} in rabbits is 2,063 mg/kg [Smyth and Carpenter 1948]. In prolonged contact with the skin, allyl chloride caused moderate irritation [Grant 1986]. The oral LD_{50} in rats is

700 mg/kg [Smyth and Carpenter 1948]. Rats, guinea pigs, rabbits, and dogs exposed to allyl chloride at 8 ppm for 7 hr/day for 1 month were asymptomatic but had liver and kidney necrosis at autopsy [Clayton and Clayton 1981]. When these animals were exposed at 3 ppm on the same regimen for 6 months, no exposure-related effects were seen at autopsy (except for reversible liver effects in female rats) [Clayton and Clayton 1981]. Allyl chloride was neurotoxic in multiple species by inhalation, gavage, and parenteral routes of administration. The neurotoxicity has been classified as a degenerative central-peripheral distal axonopathy [ACGIH 1991a]. Allyl chloride was embryotoxic and had developmental effects in rats and mice exposed by inhalation, or by oral or intraperitoneal routes of administration [NIOSH 1991]. Allyl chloride was fetotoxic in rats exposed to 300 ppm, but not in rats exposed to 30 ppm. The chemical was not fetotoxic in rabbits or embryotoxic or teratogenic in rats or rabbits following inhalation of 30 or 300 ppm for 7 hr/day on gestation days 6 to 15 (rats) or 6 to 18 (rabbits) [NLM 1992]. Allyl chloride is mutagenic in *Salmonella typhimurium* and induces gene conversions in *Saccharomyces cerevisiae* [NLM 1992]. It has also been tested for carcinogenicity in mice by several routes of exposure: gavage, skin application, and intraperitoneal injection. A nonsignificant increase in metastasizing squamous cell carcinomas was noted in the forestomachs of mice treated by gavage with doses ranging from 129 to 258 mg/kg. No skin tumors resulted from repeated skin applications; however, allyl chloride acted as an initiator in mice receiving single dermal applications in two-stage carcinogenesis assays. Mice given intraperitoneal injections of allyl chloride showed a significant increase in the incidence of lung adenomas [IARC 1985]. Rats treated by gavage with doses ranging from 55 to 71 mg/kg showed no increase in the incidence of tumors [IARC 1985]. On the basis of these studies, the International Agency for Research on Cancer (IARC) has concluded that there is insufficient evidence that allyl chloride is a carcinogen in treated animals [IARC 1985].

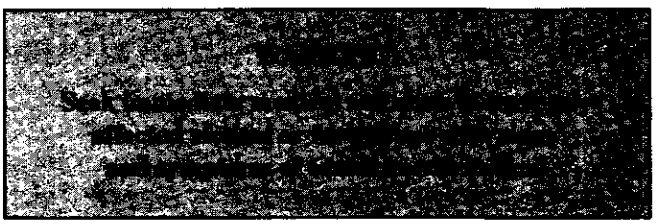
2. *Effects on Humans*: Allyl chloride is an irritant of the eyes, mucous membranes, upper respiratory tract, and skin in humans. Exposure to 25 ppm causes nasal irritation; 50 to 100 ppm causes eye irritation; and concentrations greater than these result in eye pain, conjunctivitis, sensitivity to light, and corneal burns [Grant 1986; Clayton and Clayton 1981; NLM 1992]. Exposure to saturated vapors for a few minutes can be life-threatening [NLM 1992]. Prolonged skin contact may cause a painful sensation described as a deep "bone ache" [Clayton and Clayton 1981]. Other signs and symptoms of chronic exposure have included headache, dizziness, vertigo, nausea, vomiting, proteinuria, hematuria, electrolyte elevations, increased glomerular filtration rates, severe kidney injury, and polyneuropathies [NLM 1992]. Workers exposed to concentrations of allyl chloride above 3 mg/m^3 (1 ppm) demonstrated evidence of kidney dysfunction; exposures to unspecified concentrations were reported to impart a garlic odor to the breath and skin of exposed workers and to alter the results of their liver function tests [Clayton and Clayton 1981]. Exposed female workers had decreased maximum ventilatory capacities [NLM 1992]. Workers exposed to allyl chloride concentrations ranging from 1 to 113 ppm for 16 months showed clinical signs of reversible liver damage as these signs subsided following cessation of exposure [IARC 1985]. Weakness, paresthesia, numbness, and distal neuropathy have been seen in chronically exposed workers; removal from exposure caused a reversal of their neurotoxic signs and symptoms [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Exposure to allyl chloride can cause irritation of the eyes, with redness, pain, conjunctivitis, corneal burns, and a sensitivity to light that may not be manifested for several hours after exposure; irritation of the upper respiratory tract, with coughing, difficult breathing, and delayed-onset pulmonary edema; and redness and irritation of the skin.

2. *Chronic exposure*: Exposure to allyl chloride can cause irritation of tissues including the respiratory tract mucosa, photophobia, headache, dizziness, vertigo, nausea, vomiting, dyspnea, deep bone or muscle pain caused by prolonged skin contact, and numbness, weakness, and tingling or prickly sensations in the hands and feet.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of allyl chloride. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of allyl chloride are inhaled, move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if allyl chloride or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve allyl chloride and may result in worker exposures to this substance:

—Manufacture of glycerin, epichlorohydrin, allyl alcohol, allyl amines, allyl silanes, allyl ethers of starch, and 1,2,3-trichloropropane; pharmaceuticals; polymers, plastics, and resins; perfumes; and insecticides

—Use of allyl chloride as a catalyst and modifier in the production of resins

—Use of allyl chloride in the production of barbiturates and hypnotic agents

The following methods are effective in controlling worker exposures to allyl chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to allyl chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, liver, kidneys, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific

job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to allyl chloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic eye, respiratory, liver, or kidney abnormalities.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to allyl chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of allyl chloride on the eyes, liver, kidneys, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

No biological monitoring test acceptable for routine use has yet been developed for allyl chloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to allyl chloride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne allyl chloride is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 100 liters is collected. The sample is then treated either with benzene or a mixture of carbon disulfide/dimethylformamide (99:1) to extract the allyl chloride. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method No. 1000 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If allyl chloride contacts their skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with allyl chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of allyl chloride, particularly its potential to be irritating to and absorbed by the skin.

A worker who handles allyl chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where allyl chloride or a solution containing allyl chloride is handled, processed, or stored.

STORAGE

Allyl chloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet OSHA requirements for Class IB flammable liquids [29 CFR 1910.106]. Containers of allyl chloride should be protected from physical damage and should be separated from incompatible chemicals, heat, sparks, and open flame. To prevent static sparks, metal containers and equipment used to transfer allyl chloride must be grounded and bonded. Because empty containers may still hold allyl chloride residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving allyl chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors, but do not use water spray to prevent ignition in closed spaces.

6. Prohibit contact with the material unless personnel are wearing fully effective personal protective equipment.

7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

8. Dike far ahead of large liquid spills for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether these requirements have been changed.

- **Emergency planning requirements**

Allyl chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a chemical release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for allyl chloride is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of allyl chloride per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of allyl chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although allyl chloride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of allyl chloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular

respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, face shields, aprons, boots, and body-covering clothing) should be worn to prevent skin contact with allyl chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Polyvinyl alcohol and Teflon® have been tested against permeation by allyl chloride and have demonstrated breakthrough times of 1 to 4 hr. Butyl rubber, natural rubber, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by allyl chloride.

If allyl chloride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, gas-tight goggles, or face shields should be worn during operations in which allyl chloride might contact the eyes (e.g., through splashes of solution); face shields alone, however, are not adequate for eye protection. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with allyl chloride. Contact lenses should not be worn if the potential exists for allyl chloride exposure.

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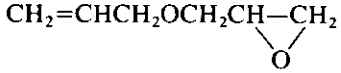
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALLYL GLYCIDYL ETHER

INTRODUCTION

This guideline summarizes pertinent information about allyl glycidyl ether (AGE) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{10}O_2$
- **Structure:**



- **Synonyms:** AGE; allyl 2,3-epoxypropyl ether; 1-(allyloxy)-2,3-epoxypropane; ((2-propenyloxy)methyl)-oxirane
- **Identifiers:** CAS 106-92-3; RTECS RR0875000; DOT 2219, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a sweet odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.16
2. Boiling point (at 760 mmHg): 154°C (309°F)
3. Specific gravity (water = 1): 0.97
4. Vapor density (air = 1 at boiling point of AGE): 3.32
5. Melting point: -100°C (-148°F)
6. Vapor pressure at 25°C (77°F): 4.7 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 14.1
8. Saturation concentration in air (approximate) at 25°C (77°F): 0.62% (6,200 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. AGE should not be exposed to light or air because explosive peroxides may be formed.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving AGE.
3. Caution: AGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 57.2°C (135°F) (open cup)
2. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
3. Class II Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

1. Odor threshold: 10 ppm
2. Evaluation of warning properties for respirator selection: Because of the lack of odor or irritant effects at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), AGE is treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for AGE is 10 parts of AGE per million parts of air (ppm) [45 milligrams of AGE per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 9.6 ppm (45 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (22 mg/m³) (Skin) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 10 ppm (44 mg/m³) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for allyl glycidyl ether

	Exposure limits ppm	mg/m³
OSHA PEL ceiling	10	45
NIOSH REL ceiling (15 min)	9.6	45
ACGIH TLV® TWA (Skin)*	5	22
STEL (Skin)	10	44

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

AGE may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**

Effects on animals: In mice and rats, acute inhalation or oral administration of AGE caused tearing, nasal discharge, dyspnea (breathing difficulty), narcosis, and death (due to pulmonary edema and central nervous system depression); acute intramuscular injection in rats produced testicular degeneration and toxic effects on the hematopoietic (blood-cell-forming) systems, including decreased leukocyte counts and atrophy of lymphoid tissue. Subchronic inhalation of AGE by rats caused central nervous system depression, reduction in weight gain, corneal opacity, pneumonia, emphysema, and enlarged adrenal glands. AGE was mutagenic in bacterial test systems.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to AGE can cause moderate irritation of the skin and severe irritation of the eyes and respiratory tract.

2. *Long-term (chronic):* Exposure to AGE can cause dermatitis with itching, swelling, and blisters. Skin sensitization to AGE and cross sensitization with other epoxy agents can also occur.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to AGE, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory, nervous, hematopoietic, and reproductive systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to AGE at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such workers. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to AGE. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and respiratory, nervous, hematopoietic, and reproductive systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination.

Any changes in the worker's health status should be compared to those expected for a suitable reference population.

• **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of AGE. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

Sampling and analysis may be performed by collecting AGE vapors with adsorption tubes of Tenax-GC resin followed by desorption with diethyl ether and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure AGE may also be used if available. A detailed sampling and analytical method for AGE may be found in the *NIOSH Manual of Analytical Methods* (method number S346).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with AGE.

Workers should be provided with and required to use splash-proof safety goggles where AGE may come in contact with the eyes.

SANITATION

Clothing which becomes contaminated with AGE should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of AGE from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of AGE's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with AGE should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle AGE should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to AGE may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for allyl glycidyl ether

Operations	Controls
During use as a reactive diluent in formulation of epoxy resins	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a copolymer for vulcanization of rubber, surface coatings, and epoxy resins	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to AGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If AGE gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to AGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If AGE gets on the skin, wash it immediately with soap and water. If AGE penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty.

Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If AGE is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing AGE, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from AGE vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing AGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. AGE should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing AGE may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for allyl glycidyl ether

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 96 ppm	Any supplied-air respirator
	Any self-contained breathing apparatus
	Any chemical cartridge respirator with organic vapor cartridge(s)
Less than or equal to 240 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 270 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
	Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Planned or emergency entry into environments containing unknown concentrations or levels above 270 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

*Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 9.6 ppm (45 mg/m^3) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ALLYL PROPYL DISULFIDE

INTRODUCTION

This guideline summarizes pertinent information about allyl propyl disulfide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{12}S_2$

- **Structure**

$CH_2{=}CHCH_2S_2C_3H_7$

- **Synonyms**

2-Propenyl propyl disulfide; onion oil; 4,5-dithia-1-octene; propyl allyl disulfide

- **Identifiers**

1. CAS No.: 2179-59-1
2. RTECS No.: JO0350000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Allyl propyl disulfide is a pale yellow, combustible liquid with a strong, pungent, irritating odor. It is the chief volatile constituent of onion oil.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 148.3
2. Boiling point (13 mm Hg): 78° to 80°C (172.4° to 176°F)
3. Specific gravity (water = 1): 0.93 at 15°C (59°F)
4. Vapor density: (air = 1 at boiling point of allyl propyl disulfide) 5.12
5. Melting point: Solidifies at −15°C (5°F)
6. Vapor pressure at 20°C (68°F): Data not available; however, this substance is known to be volatile.
7. Solubility: Insoluble in water; soluble in ether, carbon disulfide, and chloroform
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of allyl propyl disulfide with oxidizers.
3. Hazardous decomposition products: Toxic gases (such as sulfur oxides) may be released in a fire involving allyl propyl disulfide.
4. Special precautions: None known

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to allyl propyl disulfide. Other sources rate allyl propyl disulfide as a moderate fire hazard.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use foam, carbon dioxide, or dry chemical to fight fires involving allyl propyl disulfide. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1992

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for allyl propyl disulfide is 2 ppm (12 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 3 ppm (18 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (12 mg/m^3) as an 8-hr TWA and 3 ppm (18 mg/m^3) as a STEL [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned allyl propyl disulfide a threshold limit value (TLV) of 2 ppm (12 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 3 ppm (18 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• **Rationale for limits**

The limits are based on the risk of eye, nose, and upper respiratory tract irritation associated with exposure to allyl propyl disulfide.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to allyl propyl disulfide can occur through inhalation and eye or skin contact.

• **Summary of toxicology**

1. *Effects on Animals*: No studies are available on the toxicity of allyl propyl disulfide in animals.

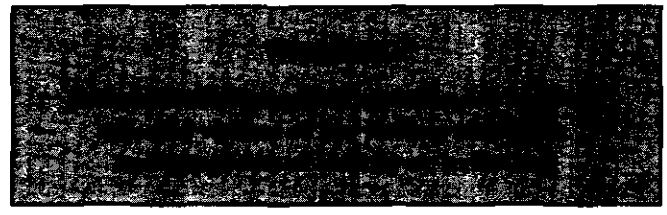
2. *Effects on Humans*: Allyl propyl disulfide irritates the eyes, nose, throat, and mucous membranes [Proctor et al. 1988]. Allyl propyl disulfide is reported to cause lacrimation at concentrations of 2 to 3 ppm and above [Grant 1986]. Workers in an onion dehydration plant who were exposed to allyl propyl disulfide at 3.4 ppm experienced eye, nose, and throat irritation [ACGIH 1991a].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to allyl propyl disulfide can cause tearing eyes, runny nose, and throat irritation.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to allyl propyl disulfide have been reported.

• **Emergency procedures**



Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to the liquid or vapors, mists, or aerosols of allyl propyl disulfide. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve allyl propyl disulfide and may result in worker exposures to this substance:

—Slicing of onions

The following methods are effective in controlling worker exposures to allyl propyl disulfide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. *Industrial ventilation—a self study* companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to allyl propyl disulfide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to allyl propyl disulfide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to allyl propyl disulfide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of allyl propyl disulfide on the respiratory system and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for allyl chloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne allyl propyl disulfide is determined by using a Chromosorb 106 tube (100/50-mg sections, 60/80 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with trichloroethylene to extract the allyl propyl disulfide. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.09 and is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If allyl propyl disulfide contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with allyl propyl disulfide should be removed.

A worker who handles allyl propyl disulfide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where allyl propyl disulfide is handled, processed, or stored.

STORAGE

Allyl propyl disulfide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of allyl propyl disulfide should be protected from physical damage and should be stored separately from oxidizers, heat, sparks, and open flame. Because containers that formerly contained allyl propyl disulfide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving allyl propyl disulfide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate the area of the spill or leak.
4. Absorb spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Allyl propyl disulfide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [40 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of allyl propyl disulfide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of allyl propyl disulfide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although allyl propyl disulfide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of allyl propyl disulfide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements

of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Safety glasses, goggles, or face shields should be worn during operations in which allyl propyl disulfide might contact the eyes (e.g., through splashes of solution).

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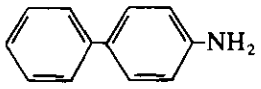
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 4-AMINODIPHENYL POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 4-aminodiphenyl for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{12}H_{11}N$
- **Structure:**



- **Synonyms:** 4-ADP; p-aminodiphenyl; 4-aminobiphenyl; 4-biphenylamine; (1,1' -biphenyl)-4-amine; diphenylamine; p-phenylaniline; xenylamine
- **Identifiers:** CAS 92-67-1; RTECS DU8925000; DOT not assigned
- **Appearance and odor:** Colorless crystals with a floral odor which turn purple on contact with air

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 169.24
2. Boiling point (at 760 mmHg): 302 °C (575.6 °F)
3. Specific gravity (water = 1): 1.160
4. Vapor density (air = 1 at boiling point of 4-aminodiphenyl): 5.8
5. Melting point: 53 °C (177 °F)
6. Solubility in water, g/100 g water at 25 °C (77 °F): 0.18

- **Reactivity**

Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving 4-aminodiphenyl.

- **Flammability**

1. Flash point: 152.7 °C (307 °F) (closed cup)
2. Autoignition temperature: 635 °C (1,175 °F)
3. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
4. Combustible solid, Flammability Rating 1 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for 4-aminodiphenyl; however, the OSHA standard requires implementation of stringent controls wherever 4-aminodiphenyl or solid or liquid mixtures containing at least 0.1% by weight or volume of 4-aminodiphenyl are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1011, 4-Aminodiphenyl. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated 4-aminodiphenyl as an A1 carcinogen (confirmed human carcinogen) (Skin). The "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. ACGIH recommends that virtually no exposure or contact by any route (i.e., respiratory, skin, or oral, as detected by the most sensitive methods) be permitted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

4-Aminodiphenyl may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* In mice, subchronic or chronic subcutaneous injection or oral administration of 4-aminodiphenyl produced cancers of the liver, bladder, or mammary glands. Chronic oral administration of 4-aminodiphenyl to dogs caused salivation, loss of body weight, blood in the urine, and bladder cancer.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

2. *Effects on humans:* Chronic exposure of workers to 4-aminodiphenyl has been associated with an increased incidence of bladder cancer.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 4-aminodiphenyl can cause headache, lethargy, urinary tract burning, blood in the urine, and bluish discoloration of the skin and mucous membranes (due to methemoglobinemia).

2. *Long-term (chronic):* Exposure to 4-aminodiphenyl can cause blood and pus in urine and frequent, painful urination.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 4-aminodiphenyl, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver and urinary tract.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 4-aminodiphenyl. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the liver. The physician should obtain baseline values for liver function tests.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 4-aminodiphenyl. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the liver and urinary tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The physician should consider use of a test which characterizes internal exposure (e.g., benzidine in urine). However, this test should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to 4-aminodiphenyl may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

Delayed-onset SHE's include bladder cancer.

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting 4-aminodiphenyl dust with glass fiber filters and silica gel tubes followed by elution with 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure 4-aminodiphenyl may also be used if available. A detailed sampling and analytical method for 4-aminodiphenyl may be found in the *NIOSH Manual of Analytical Methods* (method number 269).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe

covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting from a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower in designated facilities after the last exit of the day.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with 4-aminodiphenyl should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of 4-aminodiphenyl from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 4-aminodiphenyl's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove 4-aminodiphenyl from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1011:

Areas where 4-aminodiphenyl is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of 4-aminodiphenyl, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving 4-aminodiphenyl which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 4-aminodiphenyl into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 4-aminodiphenyl is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of 4-aminodiphenyl shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 4-aminodiphenyl from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 4-aminodiphenyl may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for 4-aminodiphenyl

Operations	Controls
During use in research and laboratory facilities	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with 4-aminodiphenyl, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 4-aminodiphenyl, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 4-aminodiphenyl gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to 4-aminodiphenyl, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 4-aminodiphenyl gets on the skin, wash it immediately with soap and water. If 4-aminodiphenyl penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If 4-aminodiphenyl is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in solid form, 4-aminodiphenyl may be collected and placed in an appropriate container.
4. For small quantities of liquids containing 4-aminodiphenyl, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation.
5. Large quantities of liquids containing 4-aminodiphenyl may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
6. 4-Aminodiphenyl dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it may then be placed in an appropriate container. Dry sweeping and dry mopping of 4-aminodiphenyl are prohibited by OSHA. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for 4-aminodiphenyl

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-AMINOPYRIDINE

INTRODUCTION

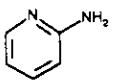
This guideline summarizes pertinent information about 2-aminopyridine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$(NH_2)C_5H_4N$

- **Structure**



- **Synonyms**

α-Aminopyridine; 1,2-dihydro-2-iminopyridine; 2-pyridylamine; o-aminopyridine; amino-2-pyridine; α-pyridinamine, 2 AP

- **Identifiers**

1. CAS No.: 504-29-0
2. RTECS No.: US1575000
3. DOT UN: 2671 55
4. DOT label: Poison

- **Appearance and odor**

2-Aminopyridine is a combustible, colorless or white, crystalline solid that has an odor described as "characteristic."

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 94.1
2. Boiling point (at 760 mm Hg): 210.6°C (411.1°F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of 2-aminopyridine): 3.2
5. Melting point: 58.1°C (136.6°F)
6. Vapor pressure at 25°C (77°F): 0.8 mm Hg
7. Solubility: Soluble in water, alcohol, benzene, ether, and acetone
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame
2. Incompatibilities: Fires and explosions may result from contact of 2-aminopyridine with strong oxidizers, strong acids, or sodium nitrate.
3. Thermal decomposition products: Toxic gases (such as oxides of nitrogen, carbon dioxide, and carbon monoxide) may be released when 2-aminopyridine burns or is heated to decomposition.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to 2-aminopyridine; other sources rate 2-aminopyridine as a moderate fire hazard.

1. Flash point: 68°C (154°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use dry chemical, carbon dioxide, or alcohol foam to extinguish fires involving 2-aminopyridine. Do not use a solid stream of water because the stream will scatter and spread the fire. However, water spray may be used to cool fire-exposed containers.

Fires involving 2-aminopyridine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of 2-aminopyridine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving 2-aminopyridine. Chemical protective clothing that is specifically recommended for 2-aminopyridine may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by 2-aminopyridine.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-aminopyridine is 0.5 part per million (ppm) parts of air (2 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 ppm (2 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-aminopyridine a threshold limit value (TLV) of 0.5 ppm (2 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of systemic poisoning associated with exposure to 2-aminopyridine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2-aminopyridine can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: 2-Aminopyridine is a dermally absorbed, central nervous system stimulant and convulsant in animals. When instilled into the eyes of rabbits, 2-aminopyridine causes only mild, reversible injury [Grant 1986]. 2-Aminopyridine is rapidly absorbed through the skin and has caused convulsions and death in guinea pigs exposed by this route [Clayton and Clayton 1981]. The acute dermal LD_{50} in guinea pigs is 0.5 ml/kg (approximately 500 mg/kg) [Clayton and Clayton 1981]. The acute oral LD_{50} is 50 mg/kg in mice and 200 mg/kg in rats. Acutely poisoned animals exhibit tremors, excitement, seizures, and tetany before death from respiratory failure [Clayton and Clayton 1981]. 2-Aminopyridine is nonmutagenic in *Salmonella typhimurium* [NLM 1992].

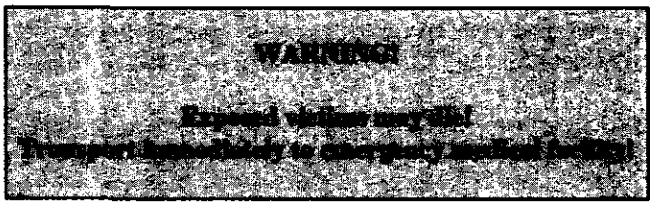
2. *Effects on Humans*: Intoxication from 2-aminopyridine can occur from inhalation of the dust or vapor or from skin absorption following direct contact. 2-Aminopyridine is a convulsant in humans and is moderately irritating to the skin and eyes [Clayton and Clayton 1981]. The lowest concentration and duration of exposure reported to be toxic in humans is 5 ppm for 5 hr; the toxic effects caused by this exposure include confusion and convulsions [NIOSH 1991]. A worker who was milling 2-aminopyridine developed high blood pressure, headache, nausea, and flushing of the extremities; subsequent air sampling demonstrated a level of 5.2 ppm; this worker had recovered completely by the following day [Clayton and Clayton 1981]. A chemical operator who continued to work for 1½ hr in clothing contaminated with 2-aminopyridine developed headache, difficult breathing, dizziness, and convulsions and died from respiratory failure [Clayton and Clayton 1981]. He may also have absorbed this substance through his skin [ACGIH 1991a]. Ingestion of as little as 60 mg in adult humans has resulted in severe poisoning, which included such signs and symptoms as: profuse sweating, burning of throat, weakness, nausea, disorientation, dizziness, thirst, ocular paresthesias, psychoticlike behavior, tremors, dyspnea, and convulsions [NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to 2-aminopyridine can cause irritation, headache, dizziness, nausea, flushing of the extremities, elevated blood pressure, weakness, difficult breathing, confusion, ocular paresthesias, seizures, and stupor. In severe poisoning, exposure to this substance may cause respiratory failure and death.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to 2-aminopyridine have been reported.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Irritation may result! ***Immediately*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: 2-Aminopyridine can cause skin irritation and can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If respirable 2-aminopyridine is inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to swab particulates from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if 2-aminopyridine or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve 2-aminopyridine and may result in worker exposures to this substance:

—Manufacture of pharmaceuticals, especially antihistamines

—Manufacture of hair dyes and other dyes

—Use of 2-aminopyridine in chemical synthesis

The following methods are effective in controlling worker exposures to 2-aminopyridine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-aminopyridine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous and respiratory systems. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-aminopyridine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history or findings consistent with seizure or other central nervous system disorders or chronic respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-aminopyridine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-aminopyridine on the central nervous and respiratory systems. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2-aminopyridine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne 2-aminopyridine is determined by using two Tenax-GC tubes in series (the first tube contains a single 35-mg section and the second tube contains a single 17-mg section; both sections are 35/60 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 12 liters is collected. The sample is then analyzed by gas chromatography using a flame ionization detector. This method is included in the OSHA Computerized Information System [OSHA 1986]. NIOSH has a similar method for analyzing 2-aminopyridine (Method S158) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Because 2-aminopyridine can be absorbed through the skin in lethal amounts, workers should immediately remove any contaminated clothing and wash thoroughly with soap and water any areas of the skin that have come in contact with this substance.

Clothing and shoes contaminated with 2-aminopyridine should be removed immediately and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of 2-aminopyridine, particularly its potential for being absorbed through the skin in lethal amounts.

A worker who handles 2-aminopyridine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where 2-aminopyridine is handled, processed, or stored.

STORAGE

2-Aminopyridine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical service in storage areas should be of explosionproof design. Containers of

2-aminopyridine should be protected from physical damage and should be stored separately from oxidizing agents, strong acids, sodium nitrate, heat, sparks, and open flame. Because empty containers may contain 2-aminopyridine residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-aminopyridine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Provide maximum explosionproof ventilation.
5. Use nonsparking tools during cleanup.
6. Carefully collect solid material and place it in a covered container for disposal.
7. To the extent feasible, avoid generating dust during cleanup.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

2-Aminopyridine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of 2-aminopyridine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of 2-aminopyridine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21–261.24. Although 2-aminopyridine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-aminopyridine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional informa-

tion on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with 2-aminopyridine. Gloves, aprons, boots, and chemical-protective suits should be worn when workers are handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2-aminopyridine permeation; however, butyl rubber has been tested against chemically similar materials (pyridines) and has demonstrated good-to-excellent resistance. Since specific test data are not available for 2-aminopyridine, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2-aminopyridine.

If 2-aminopyridine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-aminopyridine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-aminopyridine. Contact lenses should not be worn if the potential exists for 2-aminopyridine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AMITROLE

INTRODUCTION

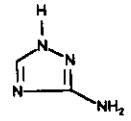
This guideline summarizes pertinent information about amitrole for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_2H_4N_4$

- **Structure**



- **Synonyms**

3-Amino-s-triazole; 2-amino-1,3,4-triazole; 3AT; ATA; aminotriazole; 3-amino-1H-1,2,4-triazole; Amitril; Amizol; Cytrol; Weedazol; Azaplant; Azolan; Diurol; Domatol; Elmasil; Emisol; Fenamine; Kleer-Lot; Orga-414; Radoxone TL; X-All Liquid; Fenavar; Ramizol; Vorox

- **Identifiers**

1. CAS No.: 61-82-5
2. RTECS No.: XZ3850000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Amitrole is a nonflammable, colorless-to-white, crystalline solid that is odorless when pure. The use of amitrole on food crops is now banned in the United States; however, this substance is still imported for use as a specialty herbicide (e.g., brush killer) and as a preharvest and postharvest herbicide on selected crops.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 84.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.14 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 159°C (318.2°F)
6. Vapor pressure at 20°C (68°F): Not applicable
7. Solubility: Soluble in water, alcohol, and chloroform; sparingly soluble in ethyl acetate; insoluble in acetone, diesel oil, ether, and kerosene
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat and light
2. Incompatibilities: Amitrole in aqueous solution is neutral, but the compound acts as a weak base to form salts in contact with acids. This substance is also mildly corrosive to iron, aluminum, copper, and copper alloys.
3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving amitrole.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to amitrole; this substance is not flammable.

1. Flash point: Not applicable

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2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing, including a self-contained breathing apparatus, when fighting fires involving amitrole.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for amitrole is 0.2 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.2 mg/m^3 as an 8-hr TWA. NIOSH has also recommended that amitrole be considered a potential occupational carcinogen and that exposure be limited to the lowest feasible concentration [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned amitrole a threshold limit value (TLV) of 0.2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The OSHA and NIOSH limits are based on the risk of cancer associated with exposure to amitrole, and the ACGIH limit is based on the risk of systemic and reproductive (fetotoxicity) effects associated with exposure to amitrole.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to amitrole can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Amitrole is a potent antithyroid agent and an animal carcinogen. Amitrole is slightly irritating to the eyes and skin of exposed rabbits [ACGIH 1991a]. Acute dermal exposure of rats and rabbits to 10,000 mg/kg did not induce toxicity. Exposure of rats to 439 mg/m^3 for 4 hr did not induce eye or respiratory tract irritation or toxicity [ACGIH 1991a]. The oral LD_{50} for mice and rats ranges from 11,000 to 14,000 mg/kg [ACGIH 1991a; Clayton and Clayton 1982]; however, a 25,000-mg/kg LD_{50} has also been cited for rats [ACGIH 1991a; NIOSH 1991]. When administered to young rabbits (dose and route not specified), amitrole produced cataracts and reduced the catalase activity within the lens [Grant 1986]. A number of subchronic studies via oral routes of administration have established the thyroid as the primary target organ of amitrole toxicity. In rats, the no observable effect level (NOEL) based on normal iodine 131 uptake was 0.5 ppm amitrole in the diet consumed during 13 weeks of exposure. Decreased thyroid function required 1.0 ppm in the diet for 29 days. Induction of increased thyroid weights required a minimum of 10 ppm in the diet for 13 weeks [ACGIH 1991a]. In addition, rats fed amitrole in drinking water (12 to 14 mg/day) developed goiter and showed histologic evidence of thyroid pathology at autopsy [Clayton and Clayton 1981]. Dietary exposure of breeding pairs of rats to amitrole caused reduced growth and viability of offspring [IARC 1986], and oral administration to pregnant mice caused fetotoxicity [NLM 1991]. In vitro mammalian test systems indicate that amitrole is also mutagenic [NIOSH 1991]. Amitrole has been tested for carcinogenicity in mice (by oral administration, skin application, and transplacental exposure), in rats (by oral and subcutaneous administration), and in hamsters (by oral administration). Orally, this substance produced thyroid tumors, liver carcinomas, and benign and malignant liver tumors in mice of both sexes; it also caused benign and malignant (adenocarcinomas) thyroid tumors in rats of both sexes, and benign pituitary tumors in female rats [IARC 1987]. On the basis of these studies, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of amitrole in animals is sufficient [IARC 1987].

2. *Effects on Humans*: Amitrole is a thyroid toxin in humans. On the basis of effects seen in animals, this substance is also a potential occupational carcinogen. There have been no reports of signs or symptoms in exposed individuals, but extrapolations from animal data suggest that dyspnea, muscle spasms, fasciculations, ataxia, anorexia, salivation, and increased body temperature could occur [NLM 1991]. A single oral dose of 100 mg of amitrole given to volunteers inhibited thyroid iodine uptake for 24 hr after administration; the volunteers included healthy persons as well as individuals with hyperthyroidism [ACGIH 1991a]. Ingestion of 20 mg/kg of a commercial preparation (30% amitrole) by a 39-year-old woman did not induce signs or symptoms of toxicity [NLM 1991]. A small cohort study of Swedish railroad workers exposed for 45 days or more to amitrole, other pesticides, and organic and inorganic chemicals revealed an excess number of deaths from cancer. A subgroup of these workers exposed both to amitrole and chlorophenoxy herbicides had an increase in cancer mortality that was statistically significant; however, in the subgroup exposed primarily to amitrole alone, no

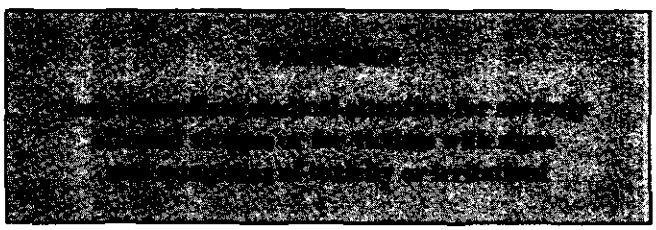
significant excess was seen [IARC 1987]. On the basis of this study, IARC has concluded that the evidence for the carcinogenicity of amitrole in humans is inadequate [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Other than mild irritation, no signs or symptoms of acute exposure to amitrole have been reported.

2. *Chronic exposure*: On the basis of effects seen in animals, the signs and symptoms of chronic exposure to amitrole could include dyspnea, muscle spasms, ataxia, anorexia, salivation, and increased body temperature; or lassitude, skin dryness, depression, and other effects indicative of thyroid function suppression.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of amitrole. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of amitrole are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if amitrole or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses involve amitrole and may result in worker exposures to this substance:

—Use in the formulation of herbicides

—Use as a herbicide for hardwood nursery stock, aquatic weeds, and nonselective weed control along highways and railroads

—Use as a cotton defoliant and as a reagent in photography

—Use as a herbicide on poison ivy and poison oak

—Use as a herbicide on food crops (now banned in the United States)

The following methods are effective in controlling worker exposures to amitrole, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to amitrole, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the thyroid gland, and they should include measurement of the individual's pre-exposure level of thyroid activity.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to amitrole at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the thyroid gland.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to amitrole exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of amitrole on the thyroid gland. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for amitrole.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to amitrole may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne amitrole is determined by using a midget impinger containing 10 ml of distilled water. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. The limit of detection for this procedure is 0.004 mg/m^3. This method is described in the OSHA Computerized Information System [OSHA 1988] and in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If amitrole contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with amitrole should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of amitrole.

A worker who handles amitrole should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where amitrole or a solution containing amitrole is handled, processed, or stored.

STORAGE

Amitrole should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of amitrole should be protected from physical damage and should be stored separately from acids, heat, and light. Because containers that formerly contained amitrole may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving amitrole, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.

2. For small dry spills, use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.

3. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

4. For large liquid spills, build dikes far ahead of the spill to contain the amitrole for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Amitrole is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State or local authorities.

The reportable quantity for amitrole is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of amitrole emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Amitrole is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U011. This substance has been banned from land disposal and may be treated by incineration. Amitrole also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of amitrole exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any possibility of skin contact with amitrole. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to amitrole permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to amitrole.

If amitrole is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which amitrole might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with amitrole. Contact lenses should not be worn if the potential exists for amitrole exposure.

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Occupational Health Guideline for Ammonia

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: NH_3
- Synonyms: Anhydrous ammonia
- Appearance and odor: Colorless gas with a penetrating, pungent, suffocating odor; it can be a liquid under pressure.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ammonia is 50 parts of ammonia per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of ammonia per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to a ceiling of 50 ppm ammonia (35 mg/m^3) averaged over a five-minute period. The NIOSH Criteria Document for Ammonia should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ammonia can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Ammonia is a severe irritant of the eyes, respiratory tract, and skin. It may cause burning and tearing of the eyes, runny nose, coughing, chest pain, cessation of respiration, and death. It may cause severe breathing difficulties which may be delayed in onset. Exposure of the eyes to high gas concentrations may produce temporary blindness and severe eye damage. Exposure of the skin to high concentrations of the gas may cause burning and blistering of the skin. Contact with liquid ammonia may produce severe eye and skin burns. Contact of the eyes, nose, throat, and skin with solutions of ammonia may produce severe burns.

2. Long-term Exposure: Repeated exposure to ammonia gas may cause chronic irritation of the eyes and upper respiratory tract.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ammonia.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ammonia at potentially hazardous levels:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ammonia causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ammonia is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examinations: The above medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Ammonia vapor is a severe irritant of the eyes, especially the cornea, the respiratory tract, and skin. Inhalation of concentrations of 2500 to 6500 ppm causes dyspnea,

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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bronchospasm, chest pain and pulmonary edema which may be fatal; production of pink frothy sputum often occurs. Consequences can include bronchitis or pneumonia; some residual reduction in pulmonary function has been reported. In a human experimental study which exposed 10 subjects to various vapor concentrations for 5 minutes, 134 ppm caused irritation of the eyes, nose, and throat in most subjects and 1 person complained of chest irritation; at 72 ppm, several reported the same symptoms; at 50 ppm, 2 reported nasal dryness and at 32 ppm only 1 reported nasal dryness. In a survey of 8 workers in a blueprint shop, ammonia concentrations of 4 to 29 ppm caused "barely noticeable" to "moderate" eye irritation; no respiratory irritation was reported. Tolerance to usually irritating concentrations of ammonia may be acquired by adaptation, a phenomenon frequently observed among workers who became inured to the effects of exposure; no data are available on concentrations that are irritating to workers who are regularly exposed to ammonia and who presumably have a higher irritation threshold. Liquid anhydrous ammonia in contact with the eyes may cause serious eye injury or blindness; on the skin it causes first- and second-degree burns which are often severe, and if extensive, may be fatal. Vapor concentrations of 10,000 ppm are mildly irritating to the moist skin, while 30,000 ppm or greater causes a stinging sensation and may produce skin burns and vesiculation. Increased cancer has been reported in workers exposed to high levels of ammonia and amines, although lack of details makes evaluation difficult.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 17
2. Boiling point (760 mm Hg): −33.4 C (-28 F)
3. Specific gravity (water = 1): Liquid 0.67 at boiling point
4. Vapor density (air = 1 at boiling point of ammonia): 0.6
5. Melting point: −77.7 C (-108 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 51
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to explode.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with calcium, hypochlorite bleaches, gold, mercury, and silver may form highly explosive products. Contact with halogens may cause violent spattering.
3. Hazardous decomposition products: None.
4. Special precautions: Liquid ammonia will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: 651 C (1204 F)
3. Flammable limits in air, % by volume: Lower: 16; Upper: 25
4. Extinguishant: Stop flow of gas.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "ammonia is a colorless gas with a characteristic odor detectable at 1 to 5 ppm."
2. Eye Irritation Level: Grant states that "ammonia is slightly irritant to human eyes at a concentration of 140 ppm in air and immediately irritating at 700 ppm."
3. Other Information: The *Hygienic Guide* states that "irritation of the respiratory tract in workers inhaling 100 ppm has been found, but 55 ppm was unobjectionable."
4. Evaluation of Warning Properties: Because of its low thresholds of odor and irritation, ammonia is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of ammonia. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ammonia may be used. An analytical method for ammonia is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid anhydrous ammonia or aqueous solutions of ammonia containing more than 10% by weight of ammonia and to prevent the skin from becoming frozen from contact with vessels containing liquid anhydrous ammonia.

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing 10% or less by weight of ammonia.

• Where there is any possibility of exposure of an employee's body to liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight should be removed immediately and not reworn until the ammonia is removed from the clothing.

• Non-impervious clothing which becomes wet with solutions containing 10% ammonia by weight or less should be removed promptly and not reworn until the ammonia is removed from the clothing.

• Clothing wet with liquid anhydrous ammonia or aqueous solutions of ammonia should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ammonia from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ammonia, the person performing the operation should be informed of ammonia's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight contacting the eyes.

• Employees should be provided with and required to use splash-proof safety goggles where solutions containing 10% ammonia by weight or less may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid anhydrous ammonia or solutions containing more than 10% ammonia by weight should be immediately washed or showered to remove any ammonia.

• Skin that becomes wet with solutions containing 10% ammonia by weight or less should be promptly washed or showered to remove any ammonia.

• Employees who handle liquid anhydrous ammonia or aqueous solutions of ammonia should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ammonia may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chemical in manufacture of fertilizers, as solvent in manufacture of textiles, leather, and pulp and paper processing; as a stabilizer in rubber manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in organic and inorganic synthesis of nitric acid, urea, plastics, fibers, synthetic resins, pharmaceuticals, pesticides, explosives, rocket fuels, cyanides, amides, dyestuffs, amines, flame retardants, and household cleaners	Process enclosure; local exhaust ventilation; personal protective equipment
Use in mining/ metallurgy ore extraction and purification, treatment of scrap metal, annealing, atomic hydrogen welding, electronics, nitriding steel	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in petroleum refining as a neutralizing agent; manufacture and recovery of cracking catalysts; and in dewaxing of lubrication oils	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a refrigerant in food installations, production of ice, cold-storage, food lockers, deicing	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during blueprinting and photography, electroplating, and as a laboratory reagent	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid anhydrous ammonia, solutions containing ammonia, or high concentrations of ammonia gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid anhydrous ammonia, strong solutions of ammonia, or high concentrations of ammonia gas get on the skin, immediately flush the contaminated skin with water. If liquid anhydrous ammonia, strong solutions containing ammonia, or high concentrations of ammonia gas penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation or burns are present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of ammonia, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When ammonia has been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the ammonia. Do not attempt to make the exposed person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If ammonia is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in liquid form, allow to vaporize.

REFERENCES

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- American Industrial Hygiene Association: "Ammonia," *Hygienic Guide Series*, Detroit, Michigan, 1971.
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- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- 'Exposure to Ammonia, Proposed Standards," *Federal Register*, 40:54684-54693, November 25, 1975.

• Manufacturing Chemists Association, Inc.: *Chemical Safety Data Sheet SD-8, Ammonia,* Washington, D.C., 1960.
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• National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . . Occupational Exposure to Ammonia,* HEW Publication No. (NIOSH) 74-136, GPO No. 017-033-00036, U.S. Government Printing Office, Washington, D.C., 1974.
• Patty, F. A. (ed.): *Toxicology,* Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
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RESPIRATORY PROTECTION FOR AMMONIA

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Gas Concentraton	
100 ppm or less	Any chemical cartridge respirator with an ammonia cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
300 ppm or less	A chemical cartridge respirator with a full facepiece and an ammonia cartridge(s).
500 ppm or less	A gas mask with a chin-style or a front- or back-mounted ammonia canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against ammonia. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ammonia; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 500 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AMMONIA

INTRODUCTION

This guideline summarizes pertinent information about ammonia for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

NH_3

- **Structure**

NH_3

- **Synonyms**

Anhydrous ammonia, ammonia gas, Am-fol, Nitro-sil, aqua ammonia, spirit of hartshorn

- **Identifiers**

1. CAS No.: 7664-41-7

2. RTECS No.: BO0875000

3. DOT UN: 1005 15 (anhydrous); 2073 15 (solutions containing more than 44% ammonia); 2672 60 (solutions containing 12% to 44% ammonia)

4. DOT labels: Poison Gas, Nonflammable Gas

- **Appearance and odor**

At room temperature, ammonia is a colorless, flammable gas; it is shipped as a liquid under its own vapor pressure. This substance has a penetrating and pungent odor. The odor threshold is reported to be 5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 17.0

2. Boiling point (at 760 mm Hg): -33.4°C (-28°F)

3. Specific gravity: 0.77 at 0°C (32°F)

4. Vapor density (air = 1 at boiling point of ammonia): 0.6

5. Melting point: -77.7°C (-107.8°F)

6. Vapor pressure at 20°C (68°F): 8,500 mm Hg

7. Solubility: Very soluble in water, alcohol, ether, and chloroform

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Under certain conditions, mixtures of ammonia and air will explode when ignited.

2. Incompatibilities: Fires and explosions may result from contact of ammonia with trimethylammonium amide, 1-chloro-2,4-dinitrobenzene, o-chloronitrobenzene, platinum, trioxygen difluoride, selenium difluoride dioxide, boron halides, acids, mercury, chlorine, iodine, bromine, hypochlorites, or chlorine bleach.

3. Hazardous decomposition products: Toxic gases (such as hydrogen gas, nitrogen gas, and nitrous oxides) may be released when ammonia decomposes.

4. Special precautions: Liquid ammonia attacks some coatings and some forms of plastic and rubber; this substance should not be allowed to contact copper, brass, bronze, or galvanized steel.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to ammonia.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Flash point: Not applicable (ammonia is a gas at room temperature).

2. Autoignition temperature: 651°C (1,204°F)

3. Flammable limits in air (% by volume): Lower, 16; upper, 25.

4. Extinguishant: Use water spray or fog.

Fires involving ammonia should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and should ventilate closed spaces before entering. Containers of ammonia may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Do not get water inside the container. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Because ammonia is highly soluble in water, dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving ammonia. Firefighters' protective clothing may not provide protection against permeation by ammonia.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ammonia is 35 ppm (27 mg/m^3) as a 15-min short-term exposure limit (STEL) [29 CFR 1910.1000, Table Z-1-A]. A STEL is a 15-min time-weighted average (TWA) exposure which should not be exceeded at any time during the workday.

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for ammonia of 25 ppm (17 mg/m^3) as an 8-hr TWA and 35 ppm as a STEL [NIOSH 1992a].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ammonia a threshold limit value (TLV) of 25 ppm (17 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek; a STEL of 35 ppm (24 mg/m^3) has been established for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of eye irritation and respiratory effects associated with exposure to ammonia. OSHA did not find it necessary to establish a TWA to protect against chronic effects. OSHA concluded that a STEL would protect against the substance's irritant effects.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ammonia can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Ammonia is a severe irritant of the eyes, respiratory tract, and skin. Liquified ammonia can induce freezing, burns, and corrosion of tissues. Exposure of guinea pigs to 5,000 to 6,000 ppm for 30 to 120 min induced blindness [AIHA 1988]. The approximate 1-hr LC_{50} for cats and rabbits was 9,900 ppm. This concentration induced severe bronchiolar damage, alveolar congestion, edema atelectasis, hemorrhage, and emphysema in the animals that died [NLM 1991]. The 4-hr LC_{50} in rats is 2,000 ppm, and the oral LD_{50} is 350 mg/kg [NIOSH 1992b]. In mice, the RD_{50} (the concentration capable of reducing respiratory rate by 50%) was approximately 300 ppm. Continued exposure for 6 hr/day for 5 days produced nasal lesions including hypertrophy, hyperplasia, epithelial erosion, ulceration, and necrosis [NLM 1991]. Continuous exposure to ammonia for several weeks at 658 ppm produced marked eye irritation in dogs and rabbits and corneal opacity in rabbits [Grant 1986]. Rats similarly exposed developed interstitial pneumonitis with calcification of the bronchi and renal tubules, epithelial proliferation of the renal tubules, myocardial fibrosis, and fatty liver [NLM 1991]. Rats, guinea pigs, dogs, rabbits, and monkeys exposed to 1,100 ppm for 8 hr/day, 5 days/week for 6 weeks showed signs of moderate eye and nasal irritation but no signs of systemic poisoning [AIHA 1988]. Although all monkeys, dogs, and rabbits survived a continuous 90-day exposure to 680 ppm, this exposure was fatal to 13 of 15 rats and 4 of 15 guinea pigs [AIHA 1988]. No clinically significant findings were detected at autopsy in rats continuously exposed to 180 ppm for 90 days [AIHA 1988; Clayton and Clayton 1981].

2. *Effects on Humans*: Ammonia gas is severely irritating to the eyes and to the moist skin and mucous membranes of humans. In contact with the eyes, liquid anhydrous ammonia causes severe damage that may lead to blindness [Proctor et al. 1988]. When in contact with the skin, liquified ammonia can cause freezing and third-degree burns [NLM 1991; Proctor et al. 1988]. Two volunteers exposed to ammonia at approximately 24 ppm showed signs of mild nasal irritation

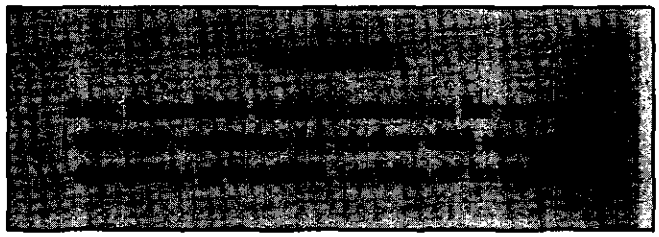
on clinical examination [Clayton and Clayton 1981]. Five of six volunteers exposed to 30 or 50 ppm for 10 min reported mild to moderate eye and upper respiratory tract irritation [Clayton and Clayton 1981]. At 130 ppm, however, volunteers experienced lacrimation and nose and throat irritation; one volunteer experienced pulmonary irritation [Clayton and Clayton 1981]. Exposure of humans to 500 ppm for 30 min caused changes in respiratory rate, and exposure to 1,720 ppm produced coughing in exposed individuals [AIHA 1988]. Accidental exposure to ammonia gas or the vapors of ammonia at high concentrations (approximately 2,500 to 6,500 ppm) for up to 2 hr induced chemical pneumonitis, burns (eyes, face, and mouth), severe local edema, dyspnea, progressive cyanosis, and death [Proctor et al. 1988; Clayton and Clayton 1981]. Death is normally caused by either suffocation or pulmonary edema [Clayton and Clayton 1981]. In near-lethal cases, residual effects may include visual impairment, decreased pulmonary function, and hoarseness [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Increasing ambient concentrations can cause contact irritation of the eyes and respiratory tract, tearing, hoarseness, violent coughing, painful breathing, impaired vision, severe eye damage, blindness, dyspnea, cyanosis, suffocation, and death. Direct contact with liquid anhydrous ammonia can cause frostbite and corrosion of the eyes and skin.

2. *Chronic exposure*: Exposure to ammonia can induce irritation of the eyes, nose, and upper respiratory tract, with coughing and difficult breathing.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: If tissue is frozen, seek medical attention ***immediately***; if tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia persists, get medical attention as soon as possible.

2. *Skin exposure*: If frostbite has occurred, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If frostbite has ***not*** occurred, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if an ammonia solution is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of ammonia may result in worker exposures to this substance:

—*Use as a soil fertilizer*

—Use in the manufacture of fertilizers; as a solvent in the manufacture of textiles, leather, and pulp and paper processing; and as a stabilizer in the manufacture of rubber

—*Use* in organic and inorganic synthesis of nitric acid, urea, plastics, fibers, synthetic resins, pharmaceuticals, pesticides, explosives, rocket fuels, cyanides, amides, dyestuffs, amines, flame retardants, household cleaners, sulfuric acid, and alkalies

—Use in mining and metallurgy, ore extraction and purification, treatment of scrap metal, annealing, atomic hydrogen welding, electronics, and nitriding of steel

—Use in petroleum refining as a neutralizing agent, in the manufacture and recovery of cracking catalysts, and in the dewaxing of lubrication oils

—Use as a commercial refrigerant in food processing, the production of ice, cold storage, and de-icing operations

—Use as a substitute for calcium in the bisulfite pulping of wood

—Use with chlorine to purify municipal and industrial water supplies

The following methods are effective in controlling worker exposures to ammonia, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations must be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ammonia, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ammonia at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ammonia exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ammonia on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ammonia.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termina-

tion. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to ammonia may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne ammonia is determined by using sulfuric-acid-impregnated carbon bead tubes (Supelco ORBO-77 tubes). Samples are collected at a maximum flow rate of 0.1 liter/min until a minimum air volume of 1.5 liters or a maximum air volume of 24 liters is collected. The samples are desorbed with deionized water and analyzed by ion chromatography. The limit of detection for this procedure is 1.5 ppm. This method is described in *OSHA Analytical Laboratory Method* ID-188 [OSHA 1988]. NIOSH has a similar method for analyzing ammonia using liquid sorbent badges and the same analytical procedure (Method 6701) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If ammonia contacts the skin, workers should immediately wash the affected areas with large quantities of water. Clothing contaminated with liquid ammonia should be removed immediately and should then be thoroughly flushed with cold water. Persons laundering contaminated clothing should be informed of the hazardous properties of ammonia, particularly its potential for skin irritation.

A worker who handles ammonia should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where ammonia or a solution containing ammonia is handled, processed, or stored.

STORAGE

Ammonia should be stored in a cool, well-ventilated, fire-resistant area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers of ammonia should be protected from physical damage and should be separated from oxidizers, combustible materials, heat, sparks, and open flame. Explosion proof electrical service must be installed in storage areas. Because containers that formerly contained ammonia may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ammonia, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not put water directly on the leak or spill area.
6. For small leaks, flood the area with cool water.
7. For large liquid spills, build dikes far ahead of the spill to contain the ammonia for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 500 lb or more of ammonia onsite must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of a hazardous substance into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is equal or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for ammonia is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of ammonia per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of ammonia emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although ammonia is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ammonia exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. If the use of respirators is necessary, the only respirators permitted are those that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves, boots, aprons, full-body suits, etc. should be worn as necessary. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against ammonia and have demonstrated good to excellent resistance: butyl rubber and Teflon®. Butyl rubber may provide more than 8 hr of resistance to permeation. Saranex® has demonstrated poor resistance to permeation by ammonia.

If ammonia is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ammonia might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ammonia.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AMMONIUM CHLORIDE FUME

INTRODUCTION

This guideline summarizes pertinent information about ammonium chloride fume for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

NH_4Cl

- **Synonyms**

Amchlor fume, ammoneric fume, ammonium muriate fume, darammon fume, sal ammonia fume, salammoniac fume, salammonite fume, salmiac fume

- **Identifiers**

1. CAS No.: 12125-02-9
2. RTECS No.: BP4550000
3. DOT UN: 9085 31
4. DOT label: None

- **Appearance and odor**

Ammonium chloride is a noncombustible, white, crystalline solid. It is odorless and somewhat hygroscopic. Ammonium chloride fume is the finely divided particulate form of this substance.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 53.5
2. Boiling point (760 mm Hg): 520°C (968°F)
3. Specific gravity (water = 1): 1.52 at 25°C (77°F)
4. Vapor density: Not applicable
5. Melting point: 350°C (662°F) sublimes
6. Vapor pressure at 160.4°C (320.7°F): 1 mm Hg
7. Solubility: Soluble in water, liquid ammonia, methanol, and ethanol; practically insoluble in acetone, ether, and ethyl acetate
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Violent reactions may result from contact of ammonium chloride fume with boron trifluoride, boron pentafluoride, iodine heptafluoride, or potassium chlorate. In the presence of alkalies, ammonia is evolved; in the presence of acids, hydrogen chloride is evolved. Ammonium chloride is also incompatible with the salts of lead or silver.
3. Hazardous decomposition products: Toxic gases and vapors (such as ammonia and hydrochloric acid) may be released in a fire involving ammonium chloride fume.
4. Special precautions: At fire temperatures, ammonium chloride fume corrodes metals.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to ammonium chloride fume. This substance is not combustible.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use water spray to reduce the fumes and irritant gases produced in a fire involving ammonium chloride. For small fires, use dry chemical, Halon®, water spray, foam, or other noncombustible material suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving ammonium chloride fume.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) for ammonium chloride fume are 10 mg/m^3 of air as an 8-hr time-weighted average (TWA) and 20 mg/m^3 as a short-term exposure limit (STEL)—the 15-min TWA that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 as an 8-hr TWA and 20 mg/m^3 as a STEL (15-min TWA) [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ammonium chloride fume a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek and 20 mg/m^3 as a STEL (15-min TWA) [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of respiratory system irritation associated with exposure to ammonium chloride fume.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to ammonium chloride fume can occur through inhalation and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Ammonium chloride is a tissue irritant and metabolic acidifying agent. Topical administration of 100 or 500 mg onto the eyes of rabbits caused severe or mild irritation, respectively [NIOSH 1991]. No animal data are available on the toxic effects of inhalation exposure to the fume of ammonium chloride. The acute oral LD_{50} in rats is 1,650 mg/kg [NIOSH 1991]. An acute lethal intravenous dose to mice induced hyperventilation, convulsions, coma, and death [NLM 1991]. During a 13-week subchronic study, 10 male rats ingested a purified diet containing 5% ammonium chloride. This metabolic acidifying agent depressed food consumption and weight. Necropsy of an animal that died during week 10 revealed hemorrhagic abdominal fluid, a blood clot in the enlarged urinary bladder, inflammation of the seminal vesicles and prostate, and haemothorax. Terminal relative kidney weights were also increased. Histopathology of selected organs demonstrated only a diffuse hyperplasia of the urinary bladders in 4 of 10 rats treated with ammonium chloride. Two males had a moderate hyperplasia, and two other males had severe hyperplasia with small papillary protrusions [NIOSH 1991; de Groot et al. 1988].

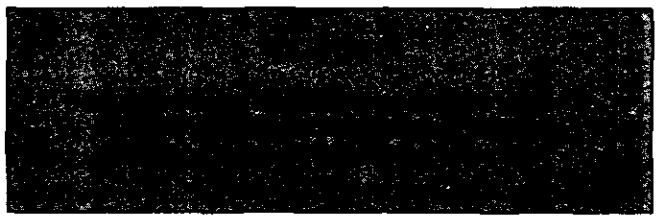
2. *Effects on Humans*: Ammonium chloride fume is a mild irritant of the eyes, nose, throat, lungs, and skin in humans. Repeated inhalation of ammonium chloride fumes (concentration unspecified) during welding also caused pulmonary sensitization in some workers [Genium 1991]. A 50-year-old woman ingested 6 g of ammonium chloride per day as a urine acidifying agent for the treatment of renal stone disease, air hunger, and profound metabolic acidosis [NLM 1991]. Ingestion of large doses of this chemical induced nausea, gastric irritation and distress, vomiting, thirst, headache, hyperventilation, progressive drowsiness, anorexia, bradycardia, mental confusion, phases of excitement, calcium-deficient tetany, tremors, hyperreflexia, and coma. Clinical chemistry analyses revealed the following adverse alterations: profound metabolic acidosis, hypokalemia, hyperchloremia, hyperglycemia, and glycosuria. EEG abnormalities have also been reported [NLM 1991].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to ambient ammonium chloride can cause irritation of contacted tissues. Ingestion exposure can cause nausea, gastric irritation and distress, vomiting, thirst, headache, hyperventilation, progressive drowsiness, anorexia, bradycardia, mental confusion, phases of excitement, calcium-deficient tetany, tremors, hyperreflexia, and coma.

2. *Chronic exposure*: Chronic exposure to ammonium chloride fume can cause difficult breathing, wheezing, and coughing in sensitized individuals.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of ammonium chloride may result in worker exposures to ammonium chloride fume:

—Use as a flux for coating sheet iron with zinc, in tinning, and in soldering

—Use in dry and Leclanche batteries

—Use in electroplating and welding

—Use in cleaning soldering irons

The following methods are effective in controlling worker exposures to ammonium chloride fume, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ammonium chloride fume, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific

job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ammonium chloride fume at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with allergies or with respiratory tract or skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ammonium chloride fume exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ammonium chloride fume on the respiratory tract and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ammonium chloride fume.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne ammonium chloride fume is determined by using a tared, low-ash polyvinyl chloride filter (5-micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing). This method has a sampling and analytical error of 0.10 and is described in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985].

PERSONAL HYGIENE

If ammonium chloride fume contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with ammonium chloride fume should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of ammonium chloride fume, particularly its potential for causing irritation.

A worker who handles ammonium chloride fume should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where ammonium chloride fume is generated.

RELEASES

In the event of a large release of ammonium chloride fume, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a release:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate potentially explosive atmospheres.
4. Use cleanup procedures such as vacuuming and wet mopping to minimize dust generation.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Ammonium chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for ammonium chloride fume is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of ammonium chloride fume emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although ammonium chloride fume is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ammonium chloride fume exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent skin contact with ammonium chloride fume. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Chlorinated polyethylene is recommended for protection against ammonium chloride.

Safety glasses, goggles, or face shields should be worn during operations in which ammonium chloride fume might

contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ammonium chloride fume. Contact lenses should not be worn if the potential exists for exposure to ammonium chloride fume.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AMMONIUM SULFAMATE

INTRODUCTION

This guideline summarizes pertinent information about ammonium sulfamate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$NH_4SO_3NH_2$

- **Synonyms**

Ammonium amidosulfonate, ammonium amidosulphate, monoammonium sulfamate, sulfamic acid, monoammonium salt, sulfamate, Ammate, Amcide, Ammat, Amicide

- **Identifiers**

1. CAS No.: 7773-06-0
2. RTECS No.: WO6125000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Ammonium sulfamate is a white, brown-gray, or colorless crystalline noncombustible solid that is odorless.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.1
2. Boiling point (at 760 mm Hg): Decomposes at 160°C (320°F)
3. Specific gravity (water = 1): 1.77
4. Vapor density: Not applicable
5. Melting point: 131°C (268°F)
6. Vapor pressure at 20°C (68°F): Zero
7. Solubility: Highly soluble in water and liquid ammonia; moderately soluble in glycerol, glycol, and formamide; slightly soluble in ethanol
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Fires and explosions may result from contact of ammonium sulfamate with strong oxidizers, hot water, potassium, sodium, sodium nitrite, metal chlorates, or hot acid solutions.
3. Hazardous decomposition products: Toxic gases (such as nitrogen or sulfur oxides and carbon monoxide) may be released when ammonium sulfamate decomposes.
4. Special precautions: Ammonium sulfamate is corrosive to mild steel.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to ammonium sulfamate; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

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Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving ammonium sulfamate.

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) for ammonium sulfamate are 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr TWAs [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ammonium sulfamate a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• **Rationale for limits**

The limits are based on the risk of physical irritation associated with exposure to ammonium sulfamate.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to ammonium sulfamate can occur through inhalation and eye or skin contact.

• **Summary of toxicology**

1. *Effects on Animals*: Ammonium sulfamate has a low order of toxicity in animals. When instilled into the eyes of rabbits, a 4% solution caused no irritation [Grant 1986]. The application of 20% to 50% solutions of ammonium sulfamate to the shaved skin of rats failed to produce irritation or systemic toxicity [ACGIH 1991a]. However, rabbits dermally exposed to 15% to 30% solutions for 20 days developed slight skin reactions [NLM 1991]. The oral LD_{50} is 2,000 mg/kg for rats and 3,100 mg/kg for mice [NIOSH 1991]. Continuous feeding studies in rats have shown that chronic ingestion of high doses of ammonium sulfamate impairs growth but produces no other adverse effects [ACGIH 1991a]. Intraperitoneal injection of 0.8 g/kg ammonium sulfamate in rats produced respiratory stimulation and prostration before death occurred [Proctor et al. 1988].

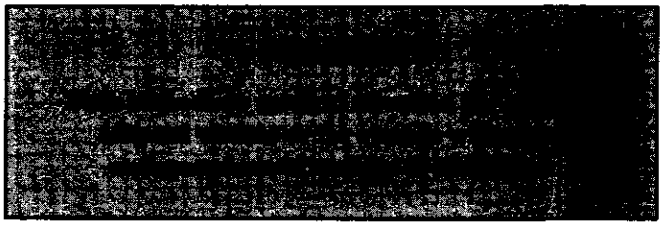
2. *Effects on Humans*: Ammonium sulfamate dust can cause irritation of the eyes, skin, and mucous membranes. Few data are available on the effects of ammonium sulfamate exposure in humans. Repeated application of a 4% solution to the forearms of five volunteers did not produce irritation [Proctor et al. 1988]. Ingestion has caused gastrointestinal disturbances.

• **Signs and symptoms of exposure**

1. *Acute exposure*: The signs and symptoms of acute overexposure to ammonium sulfamate include possible irritation of the eyes and nose, cough, gastrointestinal disturbances, respiratory stimulation, prostration, and death.

2. *Chronic exposure*: No signs or symptoms of chronic ammonium sulfamate exposure have been reported.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if ammonium sulfamate is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures

(e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve ammonium sulfamate and result in worker exposures to this substance:

—Application of ammonium sulfamate as a herbicide for control of woody plants

—Manufacture of fire-retardant compositions for flameproofing textiles and paper products

—Generation of nitrous oxide gas

—Manufacture of electroplating solutions

The following methods are effective in controlling worker exposures to ammonium sulfamate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ammonium sulfamate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and upper respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ammonium sulfamate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with drug allergies, aspirin intolerance, or eye, skin, or upper respiratory tract diseases; individuals using anticoagulant medications also may be at increased risk.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ammonium sulfamate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ammonium sul-

famate on the eyes, skin, or upper respiratory tract or on blood clotting time. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ammonium sulfamate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne ammonium sulfamate is determined by using tared, low-ash polyvinyl chloride filters (5 microns). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. This is a gravimetric field test method based on the total weight collected; therefore, the sample does not need to be submitted to the laboratory for analysis. This method is described under "Filter Weighting Procedure" in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985]. Additional information can be found in Method 348 of the *Occupational Exposure Sampling Strategy Manual* [NIOSH 1977].

PERSONAL HYGIENE

If ammonium sulfamate contacts the skin, workers should wash the affected areas with soap and water.

Clothing and shoes that are grossly contaminated with ammonium sulfamate should be removed and provisions should be made for safely removing this chemical from these articles.

A worker who handles ammonium sulfamate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where ammonium sulfamate is handled, processed, or stored.

STORAGE

Ammonium sulfamate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of ammonium sulfamate should be protected from physical damage and should be separated from strong oxidizers, water, potassium, sodium, sodium nitrite, metal chlorates, hot acid solutions, heat, sparks, and open flame. Because containers that formerly contained ammonium sulfamate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving ammonium sulfamate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate atmosphere to reduce the dust concentration.
5. Cover spills with a plastic sheet or tarp to minimize spreading; use a clean shovel to place the material into a clean, dry container; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Ammonium sulfamate is not subject to EPA's emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act

(CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for ammonium sulfamate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by SARA [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of ammonium sulfamate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although ammonium sulfamate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ammonium sulfamate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with ammonium sulfamate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to ammonium sulfamate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to ammonium sulfamate.

If ammonium sulfamate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ammonium sulfamate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ammonium sulfamate. Contact lenses

should not be worn if the potential exists for ammonium sulfamate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE

FOR n-AMYL ACETATE

INTRODUCTION

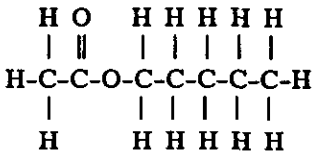
This guideline summarizes pertinent information about n-amyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CH_3COO(CH_2)_4CH_3$

- **Structure**



- **Synonyms**

Pentyl acetate, amyl acetic ester, pear oil, acetic acid, amyl ester, acetic acid, pentyl ester, amyl acetate, amyl acetic ether, pent-acetate, 1-pentanol acetate, primary amyl acetate

- **Identifiers**

1. CAS No.: 628-63-7
2. RTECS No.: AJ1925000
3. DOT UN: 1104 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

n-Amyl acetate is a flammable, colorless liquid with a bananalike odor. The odor threshold is reported to be 0.15 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.2
2. Boiling point (at 760 mm Hg): 149°C (300°F)
3. Specific gravity (water = 1): 0.88 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-amyl acetate): 4.5
5. Melting point: −70.5°C (−94.9°F)
6. Vapor pressure at 20°C (68°F): 4 mm Hg
7. Solubility: Slightly soluble in water, miscible with alcohol and ether
8. Evaporation rate (butyl acetate = 1): 0.42

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or flames
2. Incompatibilities: Fire and explosion may result from contact with nitrates, strong oxidizers, strong alkalies, or strong acids.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide), acrid smoke, and irritating fumes may be released when n-amyl acetate decomposes.
4. Special precautions: n-Amyl acetate can damage some plastics, rubbers, and coatings.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to n-amyl acetate.

1. Flash point: 25°C (77°F) (closed cup)
2. Autoignition temperature: 360°C (680°F)
3. Flammable limits in air (% by volume): Lower, 1.1; upper, 7.5

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use dry chemical, carbon dioxide, or alcohol foam to fight fires involving n-amyl acetate. Water should not be used as an extinguishant because it will spread the flames.

Fires involving n-amyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of n-amyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-amyl acetate. Firefighters' protective clothing may not provide protection against permeation by n-amyl acetate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-amyl acetate is 100 ppm (525 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 100 ppm (525 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-amyl acetate a threshold limit value (TLV) of 100 ppm (525 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation of the eyes and respiratory passages associated with exposure to n-amyl acetate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to n-amyl acetate can occur through inhalation, ingestion, or contact with the skin, eyes, and mucous membranes. n-Amyl acetate can also be absorbed slowly through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: n-Amyl acetate is an irritant of the eyes, skin, and respiratory tract in animals. When instilled into the eyes of rabbits, n-amyl acetate liquid causes mild and reversible corneal epithelial injury [Grant 1986]. When it contacts the skin, n-amyl acetate causes defatting [AIHA 1978]. The oral LD_{50} in rats is 6,500 mg/kg [NIOSH 1991]. In rabbits, the LD_{50} in a 24-hr covered skin penetration test is greater than 20 ml/kg [AIHA 1978]. All rats exposed to approximately 5,200 ppm died within 8 hr [ACGIH 1991a]. Autopsies of animals chronically exposed at 2,000 to 5,000 ppm for extended (not further specified) periods showed injury to the lungs, brain, liver, and kidneys [AIHA 1978].

2. *Effects on Humans*: n-Amyl acetate is an irritant of the eyes, skin, and mucous membranes in humans; at high concentrations, it causes narcosis. At concentrations above 300 ppm, exposure causes burning of the eyes and conjunctival hyperemia [Grant 1986]. The lowest toxic concentration reported in humans is 200 ppm for 30 min; exposure to this concentration causes eye irritation and headaches [NIOSH 1991; Proctor et al. 1988]. Prolonged or repeated skin contact with n-amyl acetate liquid causes defatting and irritation and may lead to dermatitis [AIHA 1978].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to n-amyl acetate can cause headache, dizziness, cardiac arrhythmia, narcosis, nausea, pulmonary edema, and irritation of the eyes, nose, and throat. Skin contact with liquid n-amyl acetate results in irritation, and eye contact causes irritation, redness, and a burning sensation.

2. *Chronic exposure*: Chronic exposure to n-amyl acetate can cause defatting of the skin and contact dermatitis.

- **Emergency procedures**

Keep unconscious victims warm and on their sides to avoid

choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of n-amyl acetate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of n-amyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if n-amyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve n-amyl acetate and may result in worker exposures to this substance:

—Use of n-amyl acetate as a vehicle solvent in the manufacture of cellulose nitrate lacquers, lacquer thinners, adhesives, paints, enamels, enamel removers, nitrate cements, and film cements

—Spray, hand, brush, or coating applications of paints, lacquers, lacquer thinners, film cements, enamels, adhesives, nitrate cements, and enamel removers

—Extraction of penicillin from fermentation broth during production of antibiotics

—Manufacture of photographic film, quick-drying inks, metallic inks, transfer inks, and artificial fruit-flavoring agents

—Use of n-amyl acetate as a vehicle solvent during molding operations in the manufacture of cellulose nitrate plastics, toys, eyeglass frames, combs, and novelties

—Manufacture of furniture polish, leather polish, and shoe polish

—Pre-spotting and spotting operations in the dry cleaning industry

The following methods are effective in controlling worker exposures to n-amyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures.

To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with potential for exposure to n-amyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to n-amyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to n-amyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of n-amyl acetate on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-amyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-amyl acetate is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the n-amyl acetate. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.08. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If n-amyl acetate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with n-amyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of n-amyl acetate, particularly its potential for causing irritation.

A worker who handles n-amyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where n-amyl acetate or a solution containing it is handled, processed, or stored.

STORAGE

n-Amyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of n-amyl acetate should be protected from physical damage and should be stored separately from strong oxidizers, strong alkalies, nitrates, strong acids, heat, sparks, and open flame. To prevent static sparks, metal storage containers should be bonded and electrically grounded. All tools and equipment used to open or close containers of n-amyl acetate should be of the non-

sparking type. Drums used to store n-amyl acetate must be equipped with self-closing valves, pressure-vacuum bungs, and flame arresters. Because empty containers that formerly contained n-amyl acetate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving n-amyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove any hot metal surface and all sources of heat and ignition.

4. Provide maximum explosionproof ventilation.

5. Use nonsparking tools for cleanup.

6. Absorb liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the n-amyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Amyl acetate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of a hazardous substance into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for n-amyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-amyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although n-amyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act of 1976 as amended (RCRA) [42 U.S.C. 690 et seq], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of n-amyl acetate are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous substances to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-amyl acetate exceeds

prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about selection and use of respirators and the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with n-amyl acetate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Polyvinyl alcohol has demonstrated good-to-excellent resistance to permeation by n-amyl acetate, withstanding permeation for more than 4 but fewer than 8 hr. Butyl rubber has demonstrated limited resistance to permeation. Natural rubber, neoprene, nitrile rubber, Viton®, and polyvinyl chloride have demonstrated poor resistance to permeation by n-amyl acetate.

If n-amyl acetate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which n-amyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-amyl acetate. Contact lenses should not be worn if the potential exists for n-amyl acetate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE

FOR sec-AMYL ACETATE

INTRODUCTION

This guideline summarizes pertinent information about sec-amyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_7H_{14}O_2$

- **Structure**

$CH_3COOCH(CH_3)C_3H_7$

- **Synonyms**

2-Pentyl acetate, 2-pentanol acetate, 1-methylbutyl acetate, 2-acetoxypentane

- **Identifiers**

1. CAS No.: 626-38-0
2. RTECS No.: AJ2100000
3. DOT UN: 1104 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

sec-Amyl acetate is a flammable, colorless liquid with a mild, transient, pear- or banana-like odor. The odor threshold is reported to be between 0.002 and 0.08 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.2
2. *Boiling point (at 760 mm Hg):* 121°C (249°F)
3. Specific gravity (water = 1): 0.87 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of sec-amyl acetate): 4.5
5. Melting point: -78°C (-109°F)
6. Vapor pressure at 20°C (68°F): 7 mm Hg
7. Solubility: Slightly soluble in water; soluble in alcohol and ether
8. Evaporation rate (butyl acetate = 1): 0.9

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame
2. Incompatibilities: Fires and explosions may result in contact of sec-amyl acetate with nitrates, strong oxidizers, strong alkalies, or strong acids.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released when sec-amyl acetate is heated to decomposition.
4. Special precautions: sec-Amyl acetate may soften or dissolve plastics.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to sec-amyl acetate.

1. Flash point: 32°C (89°F) (closed cup)
2. *Autoignition temperature: Data not available*

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Flammable limits in air (% by volume): Lower, 1.0; upper, 7.5

4. Extinguishant: Use dry chemical, Halon®, alcohol foam, water spray, or carbon dioxide for small fires involving sec-amyl acetate; use water spray, fog, or alcohol foam for large fires involving this substance. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving sec-amyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of sec-amyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving sec-amyl acetate. Firefighters' protective clothing may not provide protection against permeation by sec-amyl acetate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for sec-amyl acetate is 125 ppm (650 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 125 ppm (650 mg/m^3) as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned sec-amyl acetate a threshold limit value (TLV) of 125 ppm (665 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye and respiratory tract irritation associated with exposure to sec-amyl acetate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to sec-amyl acetate can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: sec-Amyl acetate is an irritant of the eyes, skin, and respiratory tract in animals; at high concentrations, this substance is a narcotic. Guinea pigs exposed to a 2,000 ppm experienced eye and nose irritation; at 5,000 ppm, these animals showed signs of narcosis and congestion of the lungs, with symptoms of incoordination occurring in 90 min and unconsciousness in 5 hr [ACGIH 1991a]. The lowest lethal concentration (LC_{Lo}) in guinea pigs is 10,000 ppm for 5 hr [NIOSH 1991]. At autopsy, acutely poisoned animals showed slight congestion of the brain, lungs, liver, and kidneys [ACGIH 1991a; Clayton and Clayton 1981]. No chronic systemic effects have been reported.

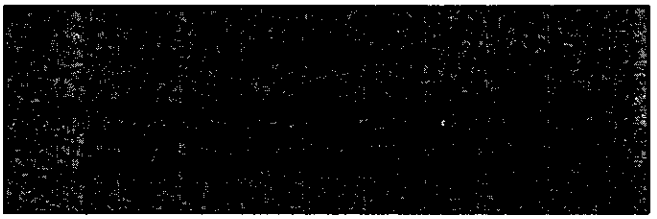
2. *Effects on Humans*: sec-Amyl acetate is an irritant of the eyes, nose, throat, and upper respiratory tract in humans. Humans exposed to 200 ppm for 3 to 5 min experienced mild eye and nose irritation and severe throat irritation [Proctor and Hughes 1978; NIOSH 1991], and exposure to 300 ppm caused bloodshot eyes [Proctor and Hughes 1978; Clayton and Clayton 1981]. An exposure to 1,000 ppm for 1 hr caused serious (not further specified) toxic effects [Proctor et al. 1988]. On the basis of effects seen in animals, exposure to high concentrations of this substance is likely to cause narcosis [Proctor et al. 1988]. Repeated exposure of the skin to liquid sec-amyl acetate causes dermatitis [Proctor and Hughes 1978]. No chronic systemic effects have been reported in humans.

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to sec-amyl acetate can cause eye irritation with pain and redness, and skin irritation and dermatitis.

2. *Chronic exposure*: Prolonged or repeated contact of the skin with sec-amyl acetate can cause defatting of the skin and dermatitis.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of sec-amyl acetate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of sec-amyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if sec-amyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve sec-amyl acetate and may result in worker exposures to this substance:

—Application of lacquers, varnishes, enamels, and metallic paints

—Use of sec-amyl acetate as a solvent for chlorinated rubber, nitrocellulose, ethyl cellulose, celluloid products, cements, coated papers, lacquers, and plastic wood

—Manufacture of artificial leather, leather-finish linoleum, photographic film, artificial silk, and furniture polish

—Manufacture of nail enamels, textile printing and sizing compounds, metallic paints, perfumes, pearlescent coatings, printing compounds, and washable wallpaper

The following methods are effective in controlling worker exposures to sec-amyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To

place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to sec-amyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may increase risk when a worker is exposed to sec-amyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic eye, skin, or respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to sec-amyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of sec-amyl acetate on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissue or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for sec-amyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne sec-amyl acetate is determined by using a solid sorbent tube containing coconut shell charcoal (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the sec-amyl acetate. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.12. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If sec-amyl acetate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with sec-amyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of sec-amyl acetate, particularly its potential to be irritating to the skin.

A worker who handles sec-amyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where sec-amyl acetate or a solution containing sec-amyl acetate is handled, processed, or stored.

STORAGE

sec-Amyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of sec-amyl acetate should

be protected from physical damage and should be stored separately from oxidizers, nitrates, strong alkalies, strong acids, heat, sparks, and open flame. To prevent static sparks, metal containers used to transfer this substance should be bonded and grounded. Only nonsparking tools should be used when handling containers of sec-amyl acetate. Because empty containers that formerly contained sec-amyl acetate may contain product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving sec-amyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use nonsparking tools for cleanup.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the sec-amyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

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A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by EPA regulations resulting from the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for sec-amyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of sec-amyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although sec-amyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of sec-amyl acetate are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of sec-amyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with sec-amyl acetate. Solvent-resistant gloves and clothing are recommended. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Polyvinyl alcohol has been tested against permeation by this substance and has demonstrated good-to-excellent resistance.

If sec-amyl acetate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which sec-amyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with sec-amyl acetate. Contact lenses should not be worn if the potential exists for exposure to sec-amyl acetate.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANILINE

INTRODUCTION

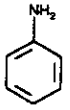
This guideline summarizes pertinent information about aniline for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_5NH_2$

- **Structure**



- **Synonyms**

Aminobenzene, aminophen, aniline oil, benzenamine, blue oil, kyanol, krystallin, cyanol, phenylamine

- **Identifiers**

1. CAS No.: 62-53-3
2. RTECS No.: BW6650000
3. DOT UN: 1547 57
4. DOT label: Poison

- **Appearance and odor**

Aniline is an oily, colorless to brown, combustible liquid that darkens on exposure to air and light. It has the characteristic aromatic amine-like odor. The odor threshold is reported to be 1.1 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 93.12
2. Boiling point (at 760 mm Hg): 184°C (363°F)
3. Specific gravity (water = 1): 1.02 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of aniline): 3.22
5. Melting point: −6.3°C (20.7°F)
6. Vapor pressure at 20°C (68°F): 0.68 mm Hg
7. Solubility: Moderately soluble in water; miscible with alcohol, benzene, chloroform, and most organic solvents
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. The vapors of aniline form explosive mixtures with air.
2. Incompatibilities: Fires and explosions may result from contact with halogens, acids (including nitric and sulfuric acids), oxidizing agents (perchlorates, peroxides, perchromates, etc.), ozone, and trichloromelamine or hexachloromelamine.
3. Hazardous decomposition products: Toxic gases (such as ammonia, carbon oxides, and nitrogen oxides) may be released when aniline is heated and/or decomposes.
4. Special precautions: Liquid aniline attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to aniline.

1. Flash point: 70°C (158°F) (closed cup)
2. Autoignition temperature: 615°C (1,139°F)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Flammable limits in air (% by volume): Lower, 1.3; upper, 11

4. Extinguishant: Use carbon dioxide, dry chemical, Halon®, water spray, or standard foam to fight fires involving aniline; never direct a solid stream of water into burning pools of liquid aniline because this will scatter and spread the fire. Water may be used to disperse vapors or to protect persons attempting to stop the leak.

Fires involving aniline should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny entry to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Cylinders of aniline may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of cylinders. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving aniline. Chemical protective clothing that is specifically recommended for aniline may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by aniline.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) PEL for aniline is 2 ppm (8 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that percutaneous absorption is a route of exposure (including mucous membranes and eyes) [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has recommended that aniline be designated a potential occupational carcinogen and that exposure be limited to the lowest feasible concentration. Contact with the worker's skin should be minimized [NIOSH 1990, 1992b].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned aniline a threshold limit value (TLV) of 2 ppm (7.6 mg/m^3) as a TWA and has also assigned aniline a "Skin" notation [ACGIH 1991b].

• Rationale for limits

OSHA and ACGIH limits are based on the risk of methemoglobinemia associated with exposure to aniline. The NIOSH cancer designation is based on significant evidence of increased bladder cancer in humans [NIOSH 1990].

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to aniline can occur through inhalation and by absorption through the eyes or skin.

• Summary of toxicology

1. *Effects on Animals*: Aniline causes methemoglobinemia in animals. Head-only versus whole-body exposure of rats for 4 hr resulted in LC_{50}s of 839 ppm and 478 ppm, respectively. These data demonstrate the significant extent to which dermal absorption occurs during ambient exposures. The dermal LD_{50} in rabbits is 820 mg/kg [NIOSH 1992a]. The oral LD_{50} in rats is 250 mg/kg, and the lowest lethal concentration in the same species is 250 ppm for 4 hr [NIOSH 1992a]. Dogs, rats, guinea pigs, and mice were exposed to 5 ppm daily for 6 months; no adverse effects were seen in these animals, except that rats developed a moderate degree of methemoglobinemia [Oberst et al. 1956]. At autopsy, rats given aniline for 5, 10, or 20 days showed splenic congestion, increased hematopoiesis, and bone marrow hyperplasia [NLM 1990]. The threshold for methemoglobinemia in rats required an exposure of 90 ppm for 4 hr. In vivo experiments with aniline induced DNA damage in the livers and kidneys of rats, and sister chromatid exchanges in the bone marrow cells of mice [NLM 1990]. In a single oral bioassay in mice and rats, aniline hydrochloride caused a significant increase in the incidence of hemangiosarcomas, sarcomas, and fibrosarcomas of the spleen and of fibrosarcomas and sarcomas of multiple body organs [NCI 1978; IARC 1987]. Based on this evidence, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of aniline in animals is limited [IARC 1987].

2. *Effects on Humans*: Exposure to aniline causes the formation of methemoglobin, which results in a functional anemia that interferes with the ability of the blood to carry oxygen. Aniline is particularly dangerous because of the ease with which this substance is absorbed by the body after inhalation of the vapors or after contact of the skin with either the vapors or liquid. The oral aniline dose estimated to be lethal to 50% of exposed individuals is between 15 and 30 g, although as little as 1 g has caused mortality [Proctor et al.

1988]. Several deaths have been reported in workers acutely poisoned by aniline; cyanosis preceded death from asphyxiation [ACGIH 1991a]. Human volunteers exposed to aniline concentrations in the range of 7 to 53 ppm showed mild signs of cyanosis; increasing the concentration to 100 or 160 ppm for 1 hr caused serious signs and symptoms [Proctor et al. 1988]. Oral administration of 25 to 65 mg to adult volunteers caused a significant dose-dependent elevation in methemoglobin in the blood [Proctor et al. 1988]. Some studies suggest that chronic exposure to low concentrations of aniline is associated with the development of anemia, digestive disturbances, lack of energy, and headache [Proctor et al. 1988]. Early studies of workers exposed to aniline and to other chemicals, including some known bladder carcinogens, showed an excess of bladder cancer deaths. Studies in workers exposed to aniline alone have shown no excess risk of bladder cancer, although these studies are generally methodologically inadequate in various respects. Based on this evidence, IARC has concluded that the epidemiologic evidence of carcinogenicity is inadequate for aniline [IARC 1987]. An epidemiologic study of workers exposed to aniline and o-toluidine showed an increased risk of bladder cancer among exposed workers [NIOSH 1989, 1990]. The effects of o-toluidine and aniline could not be separated epidemiologically.

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to aniline can induce bluish discoloration of the lips, nose, earlobes, and nailbeds; headache; weakness; irritability; drowsiness; dizziness; ringing in the ears; difficult breathing; lethargy; incoordination; rapid heart beat; and unconsciousness. The onset of these signs and symptoms may be delayed as long as 4 hr after exposure. Hemolytic anemia, jaundice, and wine-colored urine may occur after severe overexposure, and these signs may be delayed for as long as 1 week after exposure.

2. *Chronic exposure*: Chronic exposure to aniline may cause headache, anemia, gastrointestinal disturbances, and lethargy. Workers who have been exposed to aniline should be notified that they may be at increased risk of bladder cancer, and they should be alerted to its signs and symptoms. These include (1) blood in the urine, (2) other changes in the appearance of the urine, (3) changes in urinary habits, (4) lumps in the groin or lower abdomen, and (5) pain in the lower abdomen or back [NIOSH 1990].

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Immediately rinse concentrated solutions, vapors, mists, or aerosols of aniline from the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Aniline can be absorbed through the skin in lethal amounts. ***Immediately*** remove all contaminated clothing and wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If vapors, mists, or aerosols of aniline are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if aniline or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve aniline and may result in worker exposures to this substance:

—Manufacture of rigid polyurethanes; chemical synthesis of intermediates for dyestuffs and rubber processing; production of methylenediphenyl isocyanate and polymethylene polyphenylisocyanate

—Synthesis of pharmaceuticals, intermediates for pharmaceuticals, hydroquinone for photographic processing, and intermediates for agricultural chemicals

—Manufacture of cloth-marking inks, indelible inks, and lithographic and other printing inks

—Production of monomers for use in nylon fiber manufacture and synthesis of resins

—Manufacture of perfumes, varnishes, black shoe polishes, solvents, paint removers, optical whitening agents, laboratory reagents, and wood stains

The following methods are effective in controlling worker exposures to aniline, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. *Fundamentals of industrial hygiene.* Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be *monitored in a systematic program of medical surveillance* that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to aniline, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the cardiovascular system, blood, liver, and kidneys. A complete blood count also should be performed.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to aniline at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with cardiovascular system, blood, liver, or kidney diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to aniline exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of aniline on the cardiovascular system, blood, liver, and kidneys. A complete blood count should be performed. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Since aniline is a potential bladder carcinogen, exposed workers should have an annual urine analysis, including microscopic examination for microhematuria and cytologic examination for neoplastic cells [NIOSH 1990].

Biological monitoring involves sampling and analysis of body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. p-Amino-phenol, a metabolite of aniline, can be measured in the urine of exposed workers. A concentration of 50 mg of total p-aminophenol per liter of urine correlates with an airborne exposure to

2 ppm. The sample should be collected at the end of the exposure period or in the first few hours after the cessation of exposure [ACGIH 1986]. A second method of monitoring for aniline exposure is to measure the methemoglobin concentration of the blood; methemoglobinemia is the first sign of excessive aniline exposure. A methemoglobin level of 1.5% in a specimen taken at the end of the exposure period or shift is a nonspecific indicator of exposure to aniline or other methemoglobinemia-inducing agents [ACGIH 1986].

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne aniline is determined by using silica gel tubes (150/75-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 30 liters is collected. The sample is then treated with 95% ethanol to extract the aniline. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method 2002 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Incidents involving dermal exposure to aniline should be treated as an emergency. Workers should flush the affected areas immediately with plenty of water for 15 min and then thoroughly wash with soap and water. All areas of the body, including the scalp, hair, fingernails, and toenails, should be scrubbed carefully.

Clothing contaminated with aniline should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the contaminated clothing should be informed of the hazardous properties of aniline, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles aniline should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where aniline is handled, processed, or stored.

STORAGE

Aniline should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers should be inspected regularly for leakage. Containers of aniline should be protected from physical damage and should be separated from oxidizers, acids, and other incompatible chemicals, sunlight, heat, sparks, and open flame. Because containers that formerly contained aniline may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving aniline, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate atmosphere to reduce concentration.
5. Protective clothing and respiratory equipment must be worn by cleanup personnel to prevent any skin and eye contact or vapor inhalation; cleanup personnel also should work upwind or use optimum exhaust ventilation.
6. Absorb spilled material with clay, vermiculite, or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 1,000 lb or more of aniline onsite must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the

event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for aniline is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of aniline per calendar year are required [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of aniline emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Aniline is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U012. Aniline is approved for land disposal as long as its concentration in the waste or treatment residual does not exceed 14 mg/kg. Aniline may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of aniline exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Because aniline can be readily absorbed through the skin, protective clothing should be worn to prevent any possibility of skin contact with liquid aniline or aniline vapors. In work areas where there is a potential for dermal exposure to aniline, gloves, boots, aprons, and gauntlets should be worn. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by aniline and may provide protection for periods greater than 8 hr: butyl rubber and polyvinyl alcohol. Materials that may withstand permeation for more than 4 hr but fewer than 8 hr are Teflon®, Saranex®/Tynek®, and polyethylene/ethylene vinyl alcohol (e.g., 4H® or Silver Shield®). Natural rubber, neoprene, nitrile rubber, polyvinyl chloride, and Viton® have demonstrated poor resistance to

permeation by aniline. Polyethylene has questionable value as a protective material.

If aniline is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which aniline might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with aniline. Contact lenses should not be worn if the potential exists for aniline exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE

FOR ANISIDINE (o-, p-ISOMERS)

INTRODUCTION

This guideline summarizes pertinent information about anisidine (both the ortho- and the para-isomers) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

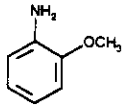
SUBSTANCE IDENTIFICATION

o-ANISIDINE

- **Formula**

$NH_2C_6H_4OCH_3$

- **Structure**



- **Synonyms**

o-Methoxyaniline, 2-methoxyaniline, 2-aminoanisole, o-anisylamine, 2-methoxybenzenamine, o-methoxyphenylamine

- **Identifiers**

1. CAS No.: 90-04-0
2. RTECS No.: BZ5410000
3. DOT UN: 2431 55
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

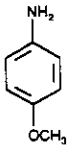
The ortho- form of anisidine is a reddish or yellowish liquid that has a characteristic amine (fishy) odor.

p-ANISIDINE

- **Formula**

$NH_2C_6H_4OCH_3$

- **Structure**



- **Synonyms**

p-Methoxyaniline, 4-methoxyaniline, 4-methoxybenzenamine, p-anisylamine, p-aminoanisole, 4-aminoanisole

- **Identifiers**

1. CAS No.: 104-94-9
2. RTECS No.: BZ5450000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

The para- form of anisidine is a light reddish-brown, fused crystalline mass that has a characteristic amine (fishy) odor.

CHEMICAL AND PHYSICAL PROPERTIES

o-ANISIDINE

- **Physical data**

1. Molecular weight: 123.2
2. Boiling point (at 760 mm Hg): 225°C (437°F)
3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-anisidine): 4.3
5. Melting point: 5°C (41°F)
6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

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7. Solubility: Practically insoluble in water; miscible with alcohol and ether

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: o-Anisidine is volatile with steam and unstable with heat.

2. Incompatibilities: Fires and explosions may result from contact with strong oxidizers.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released during the thermal decomposition of anisidine.

4. Special precautions: Liquid anisidine attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to o-anisidine.

1. Flash point: 118°C (244°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam to fight small fires involving anisidine; use water spray, fog, or standard foam to fight large fires involving anisidine.

Fires involving anisidine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of anisidine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving anisidine. Chemical protective clothing that is specifically recommended for anisidine may not provide thermal protection unless stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by anisidine.

p-ANISIDINE

- **Physical data**

1. Molecular weight: 123.2

2. Boiling point (at 760 mm Hg): 246°C (475.4°F)

3. Specific gravity (water = 1): 1.07 at 57°C (134.6°F)

4. Vapor density (air = 1 at boiling point of p-anisidine): 4.3

5. Melting point: 57°C (134.6°F)

6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

7. Solubility: Sparingly soluble in water; freely soluble in methanol, ethanol, and ether

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: p-Anisidine is unstable with heat.

2. Incompatibilities: Fires and explosions may result from contact with strong oxidizers.

3. Hazardous decomposition products (both isomers): Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released during the thermal decomposition of anisidine.

4. Special precautions: Liquid anisidine attacks some coatings and some forms of plastic and rubber.

- **Flammability**

p-Anisidine is considered a severe fire hazard, but the National Fire Protection Association has not assigned a flammability hazard rating to this chemical.

1. Flash point: 30°C (86°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon, water spray, or standard foam to fight small fires involving anisidine; use water spray, fog, or standard foam to fight large fires involving anisidine.

Fires involving anisidine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of anisidine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain

fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving anisidine. Chemical protective clothing that is specifically recommended for anisidine may not provide thermal protection unless stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by anisidine.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for anisidine (both isomers) is 0.5 mg/m^3 (0.1 ppm) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 mg/m^3 as an 8-hr TWA for both the para- and ortho-isomers. The NIOSH REL also bears a "Skin" notation. NIOSH considers the ortho-isomer to be a potential occupational carcinogen; exposure should therefore be limited to the lowest feasible concentration [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned both isomers of anisidine a threshold limit value (TLV) of 0.5 mg/m^3 (0.1 ppm) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned a "Skin" notation to anisidine [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of systemic effects associated with exposure to anisidine. NIOSH considers o-anisidine to be a potential occupational carcinogen because of positive carcinogenic results in studies of rats and mice.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to o- and p-anisidine can occur through inhalation of the dust or vapor, ingestion, or eye or skin contact. Anisidine is readily absorbed through the skin.

• Summary of toxicology

1. *Effects on Animals*: Anisidine causes methemoglobinemia and is a carcinogen in experimental animals. The toxicologic literature is often unclear about the particular isomer or mixture of isomers involved in a given study; when information about the specific form of anisidine is available, it is included in the following discussion. The oral LD_{50} in rats is 2,000 mg/kg for o-anisidine and 810 mg/kg for p-anisidine [NIOSH 1991]. Mice exposed to anisidine (isomer not specified) at 2 to 6 ppm for 2 hr/day for 1 year developed anemia and reticulocytosis [Proctor et al. 1988]. Animals that received subacute doses of either of the anisidine isomers developed anemia and other blood changes and showed signs of kidney damage at autopsy [IARC 1982]. Mice and rats fed diets containing up to 30,000 mg/kg o-anisidine hydrochloride for 7 weeks showed reductions in weight gain, and animals fed lower doses for the same period showed blackened, granular, and/or enlarged spleens [IARC 1982]. Eight-week feeding studies involving p-anisidine hydrochloride caused similar effects in rats and mice [IARC 1982]. o-Anisidine hydrochloride in the diet caused transitional-cell carcinomas of the urinary bladder in both rats and mice [IARC 1982]. The rats in this study also had statistically increased numbers of renal transitional-cell carcinomas and thyroid follicular-cell carcinomas [IARC 1982]. p-Anisidine hydrochloride did not cause cancer in mice, and the results of a carcinogenicity bioassay in rats were inconclusive [IARC 1982]. On the basis of this evidence, the International Agency for Research on Cancer (IARC) has concluded that sufficient evidence exists for the carcinogenicity of o-anisidine hydrochloride in animals but not for p-anisidine [IARC 1982].

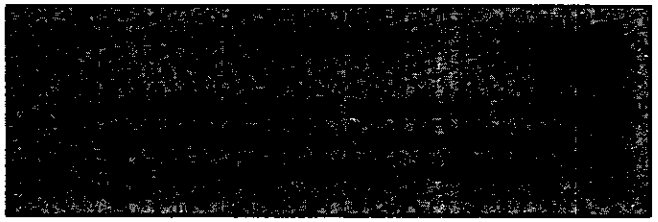
2. *Effects on Humans*: Anisidine causes methemoglobinemia in humans. Some members of a group of workers exposed to 0.4 ppm of anisidine (isomer not specified) for 6 months (3.5 hr/day) did not exhibit clinical signs of anemia but showed the following blood changes: increased methemoglobin, sulfhemoglobin, and Heinz body formation [Proctor et al. 1988]. Anisidine (form not specified) causes dermatitis on repeated or prolonged contact and is also known to be a mild skin sensitizer [Proctor et al. 1988].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to anisidine can cause methemoglobinemia, including bluish coloring of the skin, ear lobes, and lips; headache; dizziness; drowsiness; nausea and vomiting; and, in severe cases, unconsciousness and death.

2. *Chronic exposure*: Chronic exposure to anisidine can cause anemia, pallor, methemoglobinemia, fatigue, shortness of breath, and palpitations. Dermatitis and skin sensitization (which include redness and itching of the skin, blisters, swelling, and pain) may also occur. Because three cancer sites (bladder, kidney, and thyroid) have been found in animals, exposure to o-anisidine may cause cancers in humans.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of anisidine. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If the particulates, vapors, mists, or aerosols of anisidine are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to swab particulates from the nostrils

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if anisidine or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve anisidine and may result in worker exposures to this substance:

—Manufacture of azo- or triphenyl-methane dyes and intermediates

—Production of a derivative that is used as an expectorant in drugs for humans and animals and as a muscle relaxant in drugs for humans

—Preparation of organic compounds, synthesis of guaiacol and hair dyes

—Use of anisidine as a corrosion inhibitor for steel storage, as an antioxidant for some polymercaptan resins, and as a dye assist

—Use of anisidine as an analytic agent and as an intermediate in the synthesis of compounds in the form of liquid crystals

—Use of anisidine in the production of pharmaceutical and textile-processing chemicals

The following methods are effective in controlling worker exposures to anisidine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt

immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to anisidine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood, liver, kidneys, and cardiovascular system. A complete blood count, reticulocyte count, and urinalysis should be done.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to anisidine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic blood disorders, chronic liver or kidney disease, or chronic cardiovascular disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to anisidine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of anisidine on the blood, liver, kidneys, and cardiovascular system. A complete blood count, reticulocyte count, and urinalysis should be performed. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of methemoglobin in the blood is a nonspecific, qualitative indicator of exposure to a variety of chemical agents such as anisidine that induce the formation of methemoglobin. Methemoglobin levels cannot be linked quantitatively to airborne concentrations of anisidine; methemoglobin monitoring thus serves only as a screening test to identify workers who may be overexposed. A methemoglobin level of 1.5% of total hemoglobin is recommended by some sources as a biological exposure index. Blood specimens should be collected while exposure to anisidine is occurring, and, if possible, the specimens should be analyzed at the place of collection.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne anisidine (o-, p-isomers) is determined by using XAD-2 solid sorbent tubes (150/75-mg sections, 20/50 mesh). Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 320 liters is collected. The sample is then treated with methanol to extract the anisidine. Analysis is conducted by high-pressure liquid chromatography using an ultraviolet absorption detector. The limit of detection for this procedure is 0.35 μg per sample. This method is described in Method 2514 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Workers should immediately and thoroughly wash with soap and water any areas of the skin that have come in contact with the substance because anisidine can be absorbed through the skin in toxic amounts.

Clothing and shoes contaminated with anisidine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of anisidine, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles anisidine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where anisidine or a solution containing anisidine is handled, processed, or stored.

STORAGE

Anisidine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas for p-anisidine should be suitable for combustible solids. Containers of anisidine should be protected from physical damage and should be separated from oxidizing agents, heat, sparks, and open flame. Metal conveying and storage equipment should be grounded and bonded to prevent sparks. Bulk storage systems should be of explosionproof design. Because containers that formerly contained anisidine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving anisidine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Make sure that cleanup personnel wear appropriate protective clothing and equipment to prevent skin and eye contact and inhalation.
6. For small dry spills, use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the anisidine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous release, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Anisidine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of anisidine; there is no reportable quantity for anisidine.

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of anisidine emitted or released from their facility.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although anisidine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of anisidine are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if

the ambient concentration of anisidine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent any skin contact with anisidine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to anisidine permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to anisidine.

If anisidine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which anisidine dust or liquid might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with anisidine. Contact lenses should not be worn if the potential exists for anisidine exposure.

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Occupational Health Guideline for Anisidine (o,p-Isomers)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $NH_2C_6H_4OCH_3$
- Synonyms: o-Methoxyaniline; p-methoxyaniline
- Appearance and odor: Ortho: Cololorless to pink liquid with a characteristic amine odor; Para: Light red-brown solid with a characteristic amine odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for anisidine is 0.5 milligram of anisidine per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Anisidine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to anisidine may affect the ability of the blood to carry oxygen. The earliest effect may be a bluish color of the skin, especially the lips. If the lack of oxygen becomes severe, a person may have drowsiness, headache, nausea, and vomiting. If oxygen lack is very severe, it may cause unconsciousness and even death.

- **Reporting Signs and Symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to anisidine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to anisidine at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the blood, kidneys, liver, and cardiovascular system should be stressed.

—A complete blood count: Anisidine has been shown to cause methemoglobinemia and the formation of erythrocytic inclusion bodies. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

The absorption of the ortho or para isomer of anisidine, whether from inhalation of the vapor or dust or from skin absorption, causes anoxia due to the formation of methemoblobin. The peroral LD50 in rats was 1.4 g/kg. Mice repeatedly exposed to concentrations of 10 to 30 mg/m^3 for 2 hours daily showed a decrease in the excitability of nerves at the end of 1 month of exposure; after 12 months of exposure there was anemia and reticulocytosis. Workers exposed to a concentration of 1.9 mg/m3 for 3-½ hours per day for 6 months did not develop anemia or specific signs of intoxication; there were some cases of headache and vertigo, which may have been related to the observation of increased methemoglobin and sulfhemoglobin; the presence of erythrocytic inclusions, or Heinz bodies, was observed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 123

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. Boiling point (760 mm Hg): Ortho: 225 C (436 F); Para: 243 C (470 F)

3. Specific gravity (water = 1): 1.1 (both isomers)

4. Vapor density (air = 1 at boiling point of anisidine, ortho and para isomers): 4.25

5. Melting point: Ortho: 6.2 C (43 F); Para: 58.5 C (137 F)

6. Vapor pressure at 20 C (68 F): Less than 0.1 mm Hg (both isomers)

7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 1.3; Para: moderate

8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released when anisidine decomposes.

4. Special precautions: Liquid anisidine will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Para: 30 C (86 F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Foam, carbon dioxide, dry chemical

• **Warning properties**

Anisidine (o,p-isomers) is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for anisidine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with solid or liquid anisidine or liquids containing anisidine, where skin contact may occur.

• If employees' clothing may have become contaminated with solid or liquid anisidine or liquids containing anisidine, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with anisidine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of anisidine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the anisidine, the person performing the operation should be informed of anisidine's hazardous properties.

• Where exposure of an employee's body to solid or liquid anisidine or liquids containing anisidine may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with anisidine should be removed immediately and not reworn until the anisidine is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid or liquid anisidine or liquids containing anisidine may contact the eyes.

SANITATION

• Skin that becomes contaminated with anisidine should be immediately washed or showered with soap or mild detergent and water to remove any anisidine.

• Eating and smoking should not be permitted in areas where solid or liquid anisidine or liquids containing anisidine are handled, processed, or stored.

• Employees who handle solid or liquid anisidine or liquids containing anisidine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to anisidine may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of azo or triphenylmethane dyes and intermediates; use in preparation of organic compounds; in synthesis of guaicol	General dilution ventilation; personal protective equipment
Use in synthesis of hair dyes; as corrosion inhibitors for steel storage; as an antioxidant for some polymercaptan resins; and as a dyeing assist	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If anisidine gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If solid or liquid anisidine or liquids containing anisidine get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solid or liquid anisidine or liquids containing anisidine penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of anisidine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When solid or liquid anisidine or liquids containing anisidine have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If anisidine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing anisidine should be absorbed in vermiculite, dry sand, earth, or a similar material. Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal method:

Anisidine may be disposed of in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR ANISIDINE (o,p-ISOMERS)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
2.5 mg/m³ or less	Any dust and mist respirator, except single-use.
5 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	Any high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
50 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE

FOR ANISIDINE (o-, p-ISOMERS)

INTRODUCTION

This guideline summarizes pertinent information about anisidine (both the ortho- and the para-isomers) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

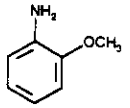
SUBSTANCE IDENTIFICATION

o-ANISIDINE

- **Formula**

$NH_2C_6H_4OCH_3$

- **Structure**



- **Synonyms**

o-Methoxyaniline, 2-methoxyaniline, 2-aminoanisole, o-anisylamine, 2-methoxybenzenamine, o-methoxyphenylamine

- **Identifiers**

1. CAS No.: 90-04-0
2. RTECS No.: BZ5410000
3. DOT UN: 2431 55
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

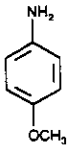
The ortho- form of anisidine is a reddish or yellowish liquid that has a characteristic amine (fishy) odor.

p-ANISIDINE

- **Formula**

$NH_2C_6H_4OCH_3$

- **Structure**



- **Synonyms**

p-Methoxyaniline, 4-methoxyaniline, 4-methoxybenzenamine, p-anisylamine, p-aminoanisole, 4-aminoanisole

- **Identifiers**

1. CAS No.: 104-94-9
2. RTECS No.: BZ5450000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

The para- form of anisidine is a light reddish-brown, fused crystalline mass that has a characteristic amine (fishy) odor.

CHEMICAL AND PHYSICAL PROPERTIES

o-ANISIDINE

- **Physical data**

1. Molecular weight: 123.2
2. Boiling point (at 760 mm Hg): 225°C (437°F)
3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-anisidine): 4.3
5. Melting point: 5°C (41°F)
6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Practically insoluble in water; miscible with alcohol and ether

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: o-Anisidine is volatile with steam and unstable with heat.

2. Incompatibilities: Fires and explosions may result from contact with strong oxidizers.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released during the thermal decomposition of anisidine.

4. Special precautions: Liquid anisidine attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to o-anisidine.

1. Flash point: 118°C (244°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam to fight small fires involving anisidine; use water spray, fog, or standard foam to fight large fires involving anisidine.

Fires involving anisidine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of anisidine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving anisidine. Chemical protective clothing that is specifically recommended for anisidine may not provide thermal protection unless stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by anisidine.

p-ANISIDINE

- **Physical data**

1. Molecular weight: 123.2

2. Boiling point (at 760 mm Hg): 246°C (475.4°F)

3. Specific gravity (water = 1): 1.07 at 57°C (134.6°F)

4. Vapor density (air = 1 at boiling point of p-anisidine): 4.3

5. Melting point: 57°C (134.6°F)

6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

7. Solubility: Sparingly soluble in water; freely soluble in methanol, ethanol, and ether

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: p-Anisidine is unstable with heat.

2. Incompatibilities: Fires and explosions may result from contact with strong oxidizers.

3. Hazardous decomposition products (both isomers): Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released during the thermal decomposition of anisidine.

4. Special precautions: Liquid anisidine attacks some coatings and some forms of plastic and rubber.

- **Flammability**

p-Anisidine is considered a severe fire hazard, but the National Fire Protection Association has not assigned a flammability hazard rating to this chemical.

1. Flash point: 30°C (86°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, Halon, water spray, or standard foam to fight small fires involving anisidine; use water spray, fog, or standard foam to fight large fires involving anisidine.

Fires involving anisidine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of anisidine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain

fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving anisidine. Chemical protective clothing that is specifically recommended for anisidine may not provide thermal protection unless stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by anisidine.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for anisidine (both isomers) is 0.5 mg/m^3 (0.1 ppm) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 mg/m^3 as an 8-hr TWA for both the para- and ortho-isomers. The NIOSH REL also bears a "Skin" notation. NIOSH considers the ortho-isomer to be a potential occupational carcinogen; exposure should therefore be limited to the lowest feasible concentration [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned both isomers of anisidine a threshold limit value (TLV) of 0.5 mg/m^3 (0.1 ppm) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned a "Skin" notation to anisidine [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of systemic effects associated with exposure to anisidine. NIOSH considers o-anisidine to be a potential occupational carcinogen because of positive carcinogenic results in studies of rats and mice.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to o- and p-anisidine can occur through inhalation of the dust or vapor, ingestion, or eye or skin contact. Anisidine is readily absorbed through the skin.

• Summary of toxicology

1. *Effects on Animals*: Anisidine causes methemoglobinemia and is a carcinogen in experimental animals. The toxicologic literature is often unclear about the particular isomer or mixture of isomers involved in a given study; when information about the specific form of anisidine is available, it is included in the following discussion. The oral LD_{50} in rats is 2,000 mg/kg for o-anisidine and 810 mg/kg for p-anisidine [NIOSH 1991]. Mice exposed to anisidine (isomer not specified) at 2 to 6 ppm for 2 hr/day for 1 year developed anemia and reticulocytosis [Proctor et al. 1988]. Animals that received subacute doses of either of the anisidine isomers developed anemia and other blood changes and showed signs of kidney damage at autopsy [IARC 1982]. Mice and rats fed diets containing up to 30,000 mg/kg o-anisidine hydrochloride for 7 weeks showed reductions in weight gain, and animals fed lower doses for the same period showed blackened, granular, and/or enlarged spleens [IARC 1982]. Eight-week feeding studies involving p-anisidine hydrochloride caused similar effects in rats and mice [IARC 1982]. o-Anisidine hydrochloride in the diet caused transitional-cell carcinomas of the urinary bladder in both rats and mice [IARC 1982]. The rats in this study also had statistically increased numbers of renal transitional-cell carcinomas and thyroid follicular-cell carcinomas [IARC 1982]. p-Anisidine hydrochloride did not cause cancer in mice, and the results of a carcinogenicity bioassay in rats were inconclusive [IARC 1982]. On the basis of this evidence, the International Agency for Research on Cancer (IARC) has concluded that sufficient evidence exists for the carcinogenicity of o-anisidine hydrochloride in animals but not for p-anisidine [IARC 1982].

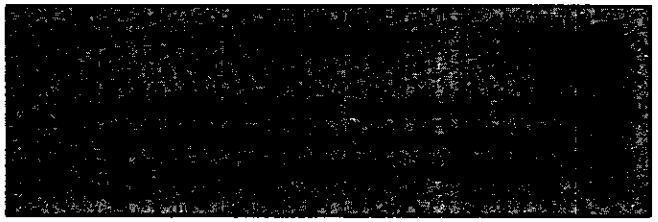
2. *Effects on Humans*: Anisidine causes methemoglobinemia in humans. Some members of a group of workers exposed to 0.4 ppm of anisidine (isomer not specified) for 6 months (3.5 hr/day) did not exhibit clinical signs of anemia but showed the following blood changes: increased methemoglobin, sulfhemoglobin, and Heinz body formation [Proctor et al. 1988]. Anisidine (form not specified) causes dermatitis on repeated or prolonged contact and is also known to be a mild skin sensitizer [Proctor et al. 1988].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to anisidine can cause methemoglobinemia, including bluish coloring of the skin, ear lobes, and lips; headache; dizziness; drowsiness; nausea and vomiting; and, in severe cases, unconsciousness and death.

2. *Chronic exposure*: Chronic exposure to anisidine can cause anemia, pallor, methemoglobinemia, fatigue, shortness of breath, and palpitations. Dermatitis and skin sensitization (which include redness and itching of the skin, blisters, swelling, and pain) may also occur. Because three cancer sites (bladder, kidney, and thyroid) have been found in animals, exposure to o-anisidine may cause cancers in humans.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of anisidine. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If the particulates, vapors, mists, or aerosols of anisidine are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to swab particulates from the nostrils

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if anisidine or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve anisidine and may result in worker exposures to this substance:

—Manufacture of azo- or triphenyl-methane dyes and intermediates

—Production of a derivative that is used as an expectorant in drugs for humans and animals and as a muscle relaxant in drugs for humans

—Preparation of organic compounds, synthesis of guaiacol and hair dyes

—Use of anisidine as a corrosion inhibitor for steel storage, as an antioxidant for some polymercaptan resins, and as a dye assist

—Use of anisidine as an analytic agent and as an intermediate in the synthesis of compounds in the form of liquid crystals

—Use of anisidine in the production of pharmaceutical and textile-processing chemicals

The following methods are effective in controlling worker exposures to anisidine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt

immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to anisidine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood, liver, kidneys, and cardiovascular system. A complete blood count, reticulocyte count, and urinalysis should be done.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to anisidine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic blood disorders, chronic liver or kidney disease, or chronic cardiovascular disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to anisidine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of anisidine on the blood, liver, kidneys, and cardiovascular system. A complete blood count, reticulocyte count, and urinalysis should be performed. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of methemoglobin in the blood is a nonspecific, qualitative indicator of exposure to a variety of chemical agents such as anisidine that induce the formation of methemoglobin. Methemoglobin levels cannot be linked quantitatively to airborne concentrations of anisidine; methemoglobin monitoring thus serves only as a screening test to identify workers who may be overexposed. A methemoglobin level of 1.5% of total hemoglobin is recommended by some sources as a biological exposure index. Blood specimens should be collected while exposure to anisidine is occurring, and, if possible, the specimens should be analyzed at the place of collection.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne anisidine (o-, p-isomers) is determined by using XAD-2 solid sorbent tubes (150/75-mg sections, 20/50 mesh). Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 320 liters is collected. The sample is then treated with methanol to extract the anisidine. Analysis is conducted by high-pressure liquid chromatography using an ultraviolet absorption detector. The limit of detection for this procedure is 0.35 μg per sample. This method is described in Method 2514 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Workers should immediately and thoroughly wash with soap and water any areas of the skin that have come in contact with the substance because anisidine can be absorbed through the skin in toxic amounts.

Clothing and shoes contaminated with anisidine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of anisidine, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles anisidine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where anisidine or a solution containing anisidine is handled, processed, or stored.

STORAGE

Anisidine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas for p-anisidine should be suitable for combustible solids. Containers of anisidine should be protected from physical damage and should be separated from oxidizing agents, heat, sparks, and open flame. Metal conveying and storage equipment should be grounded and bonded to prevent sparks. Bulk storage systems should be of explosionproof design. Because containers that formerly contained anisidine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving anisidine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Make sure that cleanup personnel wear appropriate protective clothing and equipment to prevent skin and eye contact and inhalation.
6. For small dry spills, use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the anisidine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous release, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Anisidine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of anisidine; there is no reportable quantity for anisidine.

- **Community right-to-know requirements**

Employers are not required by SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of anisidine emitted or released from their facility.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although anisidine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of anisidine are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if

the ambient concentration of anisidine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent any skin contact with anisidine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to anisidine permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to anisidine.

If anisidine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which anisidine dust or liquid might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with anisidine. Contact lenses should not be worn if the potential exists for anisidine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANTIMONY AND ITS COMPOUNDS (as Sb)

INTRODUCTION

"Antimony" is defined as elemental antimony and all antimony compounds with the exception of the gas stibine. This guideline summarizes pertinent information about antimony and its compounds for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** Sb
- **Synonyms:** Antimony regulus, stibium
- **Identifiers:** CAS 7440-36-0; RTECS CC402500; DOT 2871, label required: "St. Andrew's Cross (X)"
- **Appearance:** Silvery, white solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data for elemental antimony**

1. Molecular weight: 121.75
2. Boiling point (at 760 mmHg): 1,635 °C (2,975 °F)
3. Specific gravity (water = 1): 6.68
4. Melting point: 630.5 °C (1,116.9 °F)
5. Insoluble in water

- **Reactivity**

Incompatibilities: Oxidizing materials and acids, especially halogenated acids, can react with antimony and alloys containing antimony to produce stibine gas (antimony hydride), which is more toxic than the antimony metal alone.

- **Flammability**

1. Extinguishant: Dry graphite, sodium chloride, or potassium chloride
2. Antimony is combustible in powder form or by chemical reaction with nitrates or halogenated compounds.

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on the odor threshold and eye irritation levels, antimony should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for antimony and its compounds (as Sb) is 0.5 milligrams per cubic meter of air (mg/m^3) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for antimony and its compounds (as Sb) is 0.5 mg/m^3 as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek for antimony and its compounds (as Sb) including antimony trioxide during handling and use. The ACGIH has given antimony trioxide production an A2 designation (an A2 substance is a suspected human carcinogen) without having sufficient evidence to assign a TLV (Table 1).

Table 1.—Occupational exposure limits for antimony and its compounds

	Antimony and compounds (as Sb), mg/m^3	Antimony trioxide production, mg/m^3
OSHA PEL TWA	0.5	—
NIOSH REL TWA	0.5	—
ACGIH TLV® TWA	0.5	(A2)*

* (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Antimony may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

• **Summary of toxicology**

1. *Effects on animals:* Intraperitoneal injection of antimony or its compounds into rats produced an increase in blood eosinophil count, acute congestion of the heart, liver, and kidneys, and death (due to heart failure). Subchronic inhalation of antimony trisulfide by rats and rabbits caused degeneration of the heart muscle and changes in electrocardiograms; subcutaneous injections in rats caused fatty degeneration of the liver and swelling of kidney tubules. Chronic inhalation of antimony trioxide by guinea pigs, rats, or rabbits produced extensive lung inflammation, decreased white blood cell and eosinophil counts, enlargement of splenic follicles, and fatty degeneration of the liver.

2. *Effects on humans:* Exposure of workers to antimony trichloride, antimony trisulfide, or antimony trioxide has caused fibrosis of the lungs (pneumoconiosis), electrocardiogram changes, heart muscle changes, and death due to heart disease. Increased rates of spontaneous late abortions, premature births, and gynecologic problems have been reported for female metallurgic workers exposed to antimony trioxide, antimony pentasulfide, or metallic dust.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to antimony and its compounds can cause gastrointestinal pain, cough, loss of appetite, itching, skin eruptions, and irritation of the skin, eyes, nose, and throat.

2. *Long-term (chronic):* Exposure to antimony and its compounds can cause headache, sleeplessness, dizziness, metallic taste, ulcers, weight loss, nausea, vomiting, diarrhea, impairment of sense of smell, and pain or tightness in the chest.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include the education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include the systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to antimony, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and cardiovascular, reproductive, and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to antimony at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history and physical or other findings suggestive of cardiovascular or chronic skin disease. The physician should obtain baseline values for electrocardiographic studies appropriate for the age and medical history of the worker.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to antimony. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and cardiovascular, reproductive, and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to antimony may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

• **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to antimony should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis of antimony may be performed by collecting with a cellulose membrane filter, digesting with nitric, sulfuric, and perchloric acids, and analyzing by atomic absorption spectrophotometry. Detailed sampling and analytical methods for antimony may be found in the *NIOSH Manual of Analytical Methods* (method numbers 189 and 261).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with antimony.

Workers should be provided with and required to use dust- and splash-proof safety goggles where antimony may come in contact with the eyes.

SANITATION

Clothing which is contaminated with antimony should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of antimony from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of antimony's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with antimony should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle antimony should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to antimony may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for antimony

Operations	Controls
During crushing and transferring antimony ore	Process enclosure, dilution ventilation, and dust control with water
During production of lead/antimony alloys	Local exhaust ventilation
During machining, grinding, buffing, and polishing of metal products containing antimony	Local exhaust ventilation, personal protective clothing
During the manufacture of paints, pigments, enamels, glazes, ceramics, and glass	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to antimony, an eye-wash fountain should be provided within the immediate work area for emergency use.

If antimony gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to antimony, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If antimony gets on the skin, wash it immediately with soap and water. If antimony penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If antimony is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquids containing antimony, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing antimony may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. If in solid form, antimony may be collected and placed in an appropriate container.
5. Antimony may be collected by vacuuming with an appropriate system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal of antimony and its compounds are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for antimony and its compounds

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5.0 mg/m³	Any dust and mist respirator except single-use and quarter-mask respirators, if not present as fume
	Any supplied-air respirator
	Any self-contained breathing apparatus
Less than or equal to 12.5 mg/m³	Any powered air-purifying respirator with dust and mist filter, if not present as fume
	Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 25 mg/m³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter
	Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 80 mg/m³	Any supplied-air respirator with a full half-mask and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 80 mg/m³	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.5 mg/m³ (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ANTU

INTRODUCTION

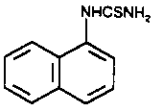
This guideline summarizes pertinent information about ANTU for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{11}H_{10}N_2S$

- **Structure**



- **Synonyms**

α-Naphthylthiourea, 1-naphthalenylthiourea, 1-(1-naphthyl)-2-thiourea, 1-naphthylthiourea, α-naphthylthiocarbamide, Alrato, Anturat, Bantu, Dirax, Kill Kantz, Krysid, Naphtox, Rattrack, Rat-tu, Smeesana

- **Identifiers**

1. CAS No.: 86-88-4
2. RTECS No.: YT9275000
3. DOT UN: 1651 53
4. DOT label: Poison

- **Appearance and odor**

ANTU is a colorless, white, or gray crystalline compound that is odorless. Commercial ANTU preparations are often contaminated with as much as 2% 2-naphthylamine, a recognized human carcinogen. ANTU is no longer manufactured in the United States.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 202.3
2. Boiling point (at 760 mm Hg): Decomposes
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of ANTU): 6.99
5. Melting point: 198°C (388.4°F)
6. Vapor pressure at 20°C (68°F): Nearly zero
7. Solubility: Practically insoluble in water, fairly soluble in hot alcohol, and soluble in acetone and triethylene glycol
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Fires and explosions may result from contact of ANTU with strong oxidizers; ANTU also reacts with silver nitrate.
3. Hazardous decomposition products: Toxic gases (such as sulfur dioxide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving ANTU.
4. Special precautions: None

- **Flammability**

ANTU may burn, but it will not ignite readily.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam to fight small fires involving ANTU; use water spray, fog, or standard foam to fight large fires involving ANTU.

Fires involving ANTU should be fought upwind and from the maximum distance possible. Isolate the hazard area and

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving ANTU. Firefighters' protective clothing may not provide protection against permeation by ANTU.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for ANTU is 0.3 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for ANTU of 0.3 mg/m^3 as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ANTU a threshold limit value (TLV) of 0.3 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of pulmonary effects associated with exposure to ANTU.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to ANTU can occur through inhalation, ingestion, and eye or skin contact; by analogy with other thiourea products, percutaneous absorption of ANTU is likely.

- **Summary of toxicology**

1. *Effects on Animals*: ANTU causes pulmonary edema and pleural effusion in exposed animals. The toxicity of ANTU varies widely among different species of animals but is especially high in adult Norway rats [Hayes 1982]. The oral LD_{50} is 6 mg/kg in rats and 4,250 mg/kg in monkeys [NIOSH 1991]. Sixty percent of rats fed a 35-mg/kg dose of ANTU died; their autopsies revealed interstitial pulmonary edema and pericardial effusions as well as mild liver damage [Proctor et al. 1988]. Rats given lethal doses of ANTU also showed increases in blood sugar, decreases in liver glycogen stores, decreased or absent urine output, and lesions of the kidney at autopsy [Gosselin et al. 1984]. After repeated doses, animals developed a tolerance to the acute toxicity of ANTU [Proctor et al. 1988]. ANTU may have antithyroid properties when administered to animals in sublethal, chronic doses [Gosselin et al. 1984]. ANTU is mutagenic in several in vitro assay systems [Hayes 1982; NIOSH 1991]. Carcinogenicity bioassays in two strains of mice were negative [Hayes 1982].

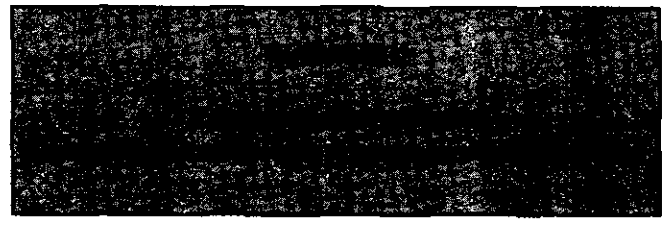
2. *Effects on Humans*: ANTU is believed to have caused bladder cancer in workers exposed during the application of ANTU-containing rodenticides; however, the causative agent in these cancers may have been β-naphthylamine, which was present in ANTU as an impurity [Orjelick 1975]. A total of 14 cases of urothelial tumors were reported [Davies et al. 1982]. When ingested, ANTU is probably not toxic to humans except in relatively large amounts; on the basis of the results of acute toxicity testing in monkeys, the mean lethal oral dose in humans is estimated to be 4 g/kg [Gosselin et al. 1984]. No reported cases have involved the ingestion of pure ANTU, but accidental or suicidal ingestions of ANTU in combination with other rat poisons have been reported. One man ingested 80 g of a rat poison that contained 30% ANTU and then drank a large amount of alcohol; he subsequently showed the following ANTU-related effects: vomiting, difficult breathing, cyanosis, and fluid in the lungs [Gosselin et al. 1984]. ANTU is reported to have caused contact eczema in one occupationally exposed worker [Hayes 1982]. Workers handling products containing thiourea (such as ANTU) have shown dermal absorption and destructive changes of the thyroid gland [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute inhalation exposure may produce coughing, lung edema, dyspnea, trenchitis, or pneumonitis [NLM 1991]. Ingestion of ANTU can induce vomiting, difficult breathing, blueness of the skin and mucous membranes, and lung edema. Tissue contact can cause eye or skin irritation.

2. *Chronic exposure*: ANTU can cause blood or pus in the urine, pain on urination, and other signs and symptoms of bladder cancer. Hypothyroidism with weight gain, dryness of the skin, eczema, and bradycardia have also been associated with occupational exposure to ANTU.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: ANTU can be absorbed through the skin in lethal amounts. ***Immediately*** remove all contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of ANTU are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if ANTU or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations involve ANTU and may result in worker exposures to this substance:

—Manufacture of ANTU

—Formulation and use of ANTU as a rodenticide to control the Norway rat

The following methods are effective in controlling worker exposures to ANTU, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to ANTU, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the thyroid and adrenal glands, respiratory tract, liver, and bladder. Medical monitoring for respiratory disease should

be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to ANTU at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with chronic respiratory disease, hypothyroidism, other endocrine disease, chronic liver disease, or bladder disorders.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to ANTU exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ANTU on the lungs, thyroid, adrenal gland, liver, and bladder. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for ANTU.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because exposure to ANTU may cause diseases with long latencies, medical surveillance may need to be continued long after job termination.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne ANTU is determined by using a 37-mm, 1-micron polytetrafluoroethylene filter. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 480 liters is collected. The samples are desorbed with methanol. Analysis is conducted by high-performance liquid chromatography using an ultraviolet light detector. The limit of detection for this procedure is 5 µg per sample. This method is described in Method No. S276 of the *NIOSH Manual of Analytical Methods* [NIOSH 1978].

PERSONAL HYGIENE

Because ANTU can be absorbed through the skin in toxic amounts, workers should dust off any solid ANTU from their skin, flush the affected areas immediately with plenty of water for 15 min, and then wash the area twice with soap and water.

Clothing and shoes contaminated with ANTU should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of ANTU, particularly its potential to be hazardous to the respiratory system, bladder, and endocrine system.

A worker who handles ANTU should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where ANTU or a solution containing ANTU is handled, processed, or stored.

STORAGE

ANTU should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of ANTU should be protected from physical damage and should be separated from strong oxidizers, heat, sparks, and open flame. Because empty containers may contain ANTU residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ANTU, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete.

The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the atmosphere to reduce the concentration of ANTU.

4. For small dry spills, use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area.

5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the ANTU for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether these requirements have been changed.

- **Emergency planning requirements**

If 10,000 lb or more of ANTU is present, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30]. If ANTU is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 5,000 lb or more is present at the facility.

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for ANTU is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of ANTU emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. ANTU is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P072. This substance has been banned from land disposal and may be treated by incineration. ANTU may also be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of ANTU exceeds prescribed exposure limits. Respirators may be used

(1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with ANTU. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to ANTU permeation; however, one source recommends polyethylene to protect against permeation by ANTU. Since specific test data are not available for ANTU, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to ANTU.

If ANTU is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which ANTU might contact the eyes (e.g., through dust particles or splashes of ANTU-containing solutions). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with ANTU. Contact lenses should not be worn if the potential exists for ANTU exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR INORGANIC ARSENIC AND ITS COMPOUNDS (as As) POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

"Inorganic arsenic" is defined as elemental arsenic and all of its inorganic compounds except arsine (see guideline for arsine). This guideline summarizes pertinent information about inorganic arsenic for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for elemental arsenic.

- **Formula:** As
- **Synonyms:** Arsenic black, arsenic-75, arsenic solid, arsenic metallic, arsenicals, grey arsenic
- **Identifiers:** CAS 7440-38-2; RTECS CG0525000; DOT 1558, label required: "Poison"
- **Appearance and odor:** Gray metal with an odor like garlic when heated

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for elemental arsenic.

- **Physical data**

1. Molecular weight: 74.92
2. Boiling point (at 760 mmHg): 613°C (1,135°F), sublimes
3. Specific gravity (water = 1): 5.73
4. Vapor density (air = 1 at sublimation point of arsenic): 2.6
5. Melting point: Sublimes at 613°C (1,135°F)
6. Insoluble in water

- **Reactivity**

1. Incompatibilities: Oxidizing agents and heat
2. Hazardous decomposition products: Toxic gases and vapors or fumes (e.g., arsenic oxide fume) may be released in a fire involving arsenic.
3. Caution: Hydrogen gas can react with inorganic arsenic to form arsine.

- **Flammability**

1. Extinguishant: All firefighting agents, except soda-acid
2. Caution: Arsenic is combustible in powder form or by chemical reaction with powerful oxidizers such as bromates, chlorates, iodates, and peroxides.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for inorganic arsenic (except arsine) is 0.01 milligrams of arsenic per cubic meter of air (mg/m^3) as a time-weighted average (TWA) over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that arsenic and all its inorganic compounds be controlled and handled as potential human carcinogens in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) for arsenic and all its inorganic compounds is 0.002 mg/m^3 as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for soluble arsenic compounds is 0.2 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek. The ACGIH has designated arsenic trioxide production as A2 (suspected human carcinogen) without having sufficient evidence to assign a TLV® (Table 1).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Inorganic arsenic compounds may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for inorganic arsenic and its compounds (as As)

	Arsenic and its inorganic compounds	Arsenic compounds, soluble	Arsenic trioxide production
	mg/m³	mg/m³	mg/m³
OSHA PEL TWA	0.01	—	—
NIOSH REL (Ca)*			
Ceiling (15 min)	0.002	—	—
ACGIH TLV® (TWA)	—	0.2	(A2)†

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected human carcinogen.

• Summary of toxicology

1. *Effects on animals:* Chronic ingestion or inhalation of inorganic arsenic by rats caused marked enlargement of the common bile duct and fatty degeneration of the liver. Injection of arsenic in pregnant rats, mice, and hamsters caused malformations of the offspring.

2. *Effects on humans:* Inhalation, ingestion, or dermal exposure of workers to inorganic arsenic has caused peripheral nerve inflammation (neuritis) and degeneration (neuropathy), reduced peripheral circulation, anemia, increased mortality due to cardiovascular failure, and cancers of the skin, lungs, and lymphatic system.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to inorganic arsenic can cause nausea, vomiting, diarrhea, weakness, loss of appetite, cough, chest pain, giddiness, headache, and breathing difficulty (dyspnea).

2. *Long-term (chronic):* Exposure to inorganic arsenic can cause weakness, nausea, vomiting, diarrhea, skin and eye irritation, hyperpigmentation, thickening of the palms and soles (hyperkeratosis), contact dermatitis, skin sensitization, warts, ulceration and perforation of the nasal septum, and numbness and weakness in the legs and feet.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevent environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to inorganic arsenic, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, peripheral nervous system, liver, lymphatic and hematopoietic (blood cell forming) systems, and respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to inorganic arsenic and its compounds at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis or peripheral neuropathy, a history and other findings consistent with chronic disease of the skin or nervous system, and significant breathing impairment due to preexisting chronic lung disease.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to inorganic arsenic. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, blood, lymphatic system, peripheral nervous system, liver, and respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH

and ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to inorganic arsenic and its compounds may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

Delayed-onset SHE's include: Inflammatory and toxic neuropathy, agranulocytosis or neutropenia (absense or a severe decrease in the number of certain white blood cells), and cancers of the liver and respiratory tract.

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling concentration evaluation

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of inorganic arsenic. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

• Method

Sampling and analysis may be performed by collecting particulate inorganic arsenic with cellulose membrane filters followed by digestion with acid and analysis by atomic absorption with flame arsine generation. A detailed sampling and analytical method may be found in the *NIOSH Manual of Analytical Methods* (method number 7900).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with inorganic arsenic.

SANITATION

Clothing which is contaminated with inorganic arsenic should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of inorganic arsenic from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of inorganic arsenic's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with inorganic arsenic should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle inorganic arsenic should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to inorganic arsenic may occur and control methods which may be effective in each case are listed in Table 2.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to inorganic arsenic, an eyewash fountain should be provided within the immediate work area for emergency use.

If inorganic arsenic gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to inorganic arsenic, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If inorganic arsenic gets on the skin, wash it immediately with soap and water. If inorganic arsenic penetrates the clothing, remove the clothing promptly and wash the skin with soap and water. Get medical attention promptly.

Table 2.—Operations and methods of control for inorganic arsenic

Operations	Controls
During the manufacture of insecticides, weed killers and fungicides; during use as a wood preservative	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the manufacture and handling of calcium arsenate; during use in the manufacture of electrical semiconductors, diodes, and solar batteries	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a bronzing or decolorizing addition in glass manufacturing; during use in the production of opal glass and enamels	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an addition to alloys to increase hardening and heat resistance	Process enclosure, local exhaust ventilation, personal protective equipment
During smelting of ores	Local exhaust ventilation, personal protective equipment

• **Rescue**
If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If inorganic arsenic or its compounds are spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities of liquids containing inorganic arsenic, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing inorganic arsenic may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Inorganic arsenic dust may be collected by vacuuming with an appropriate high-efficiency fitration system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for inorganic arsenic

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted acid gas canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ARSINE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about arsine for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines. For information on other arsenic compounds, see guideline for inorganic arsenic.

SUBSTANCE IDENTIFICATION

- **Formula:** AsH_3
- **Synonyms:** Arsenic hydride, arsenic trihydride, hydrogen arsenide
- **Identifiers:** CAS 7784-42-1; RTECS CG6475000; DOT 2188, label required: "Poison, Flammable Gas"
- **Appearance and odor:** Colorless gas with a faint odor like garlic

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 77.95
2. Boiling point (at 760 mmHg): -62.5°C (-80.5°F)
3. Vapor density (air = 1 at boiling point of arsine): 2.69
4. Melting point: -116°C (-177°F)
5. Vapor pressure at 20°C (68°F): >1 atm
6. Solubility in water, g/100 g water at 20°C (68°F): 0.07
7. Ionization potential: 10.03 eV

- **Reactivity**

1. Incompatibilities: Arsine reacts with strong oxidizers, especially chlorine and nitric acid. Arsine decomposes at temperatures above 300°C (572°F) to form elemental arsenic and hydrogen. In the presence of moisture, decomposition may be triggered by light.
2. Hazardous decomposition products: Toxic fumes may be released in a fire involving arsine.

- **Flammability**

Flammable gas

- **Warning properties**

1. Odor threshold: 0.5 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for arsine is 0.05 parts of arsine per million parts of air (ppm) [0.2 milligrams of arsine per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that arsenic and all its inorganic compounds including arsine be regarded as potential human carcinogens in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) for arsine is 0.002 mg/m^3 (as arsenic) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.05 ppm (0.2 mg/m^3) for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for arsine

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA	0.05	0.2
NIOSH REL (as arsenic) ceiling (15 min) (Ca)*	—	0.002
ACGIH TLV® TWA	0.05	0.2

* (Ca): NIOSH recommends treating as a potential human carcinogen.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• Routes of exposure

Arsine may cause adverse health effects following exposure via inhalation.

• Summary of toxicology

Effects on humans: Acute inhalation of arsine has caused the breakdown of red blood cells and hemoglobin, impairment of kidney function, damage to the liver and heart, electroencephalogram abnormality (elevation of T-waves), hemolytic anemia, and death due to kidney or heart failure. The human carcinogenic potential of arsine itself has not been determined; however, inorganic arsenic, a recognized human carcinogen in the workplace, is used in the production of arsine.

• Signs and symptoms of exposure

Short-term (acute): Exposure to arsine can cause the delayed onset of headache, malaise, weakness, dizziness, breathing difficulty (dyspnea), abdominal pain, nausea, vomiting, jaundice, bloody urine followed by absence of urination, pulmonary edema, and coma.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to arsine, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiological and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and and integrity of the skin, liver, kidneys, and lymphatic and hematopoietic (blood cell forming), respiratory, and peripheral nervous systems. A complete blood count with a reticulocyte count should be performed. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to arsine at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis or peripheral neuropathy, a history and other findings consistent with chronic disease of the skin or nervous system, and significant breathing impairment due to preexisting chronic lung disease.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to arsine. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, liver, kidneys, and hematopoietic, lymphatic, respiratory, and peripheral nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to arsine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

1. Acute SHE's include: Non-autoimmune hemolytic anemia and acute renal (kidney) failure
2. Delayed-onset SHE's include: Chronic renal (kidney) failure (see also SHE's for inorganic arsenic and its compounds)

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of arsine. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by workers) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

• **Method**

Sampling and analysis may be performed by collecting arsine using charcoal tubes with prefilters to capture particulates followed by desorption with nitric acid and analysis by atomic absorption spectrophotometry with heated graphite atomization. Direct-reading devices calibrated to measure arsine may also be used if available. A detailed sampling and analytical method for arsine may be found in the *NIOSH Manual of Analytical Methods* (method number 6001).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate clothing necessary to prevent skin contact with arsine.

SANITATION

Clothing which is contaminated with arsine should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of arsine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of arsine's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle arsine should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

Contact lenses should not be worn when there is a potential for exposure to arsine.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to arsine may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for arsine

Operations	Controls
During the manufacture of electrical semiconductors and gallium arsenide; during the manufacture, storage, and distribution of arsine	Process enclosure, local exhaust ventilation, personal protective equipment
During the refining of of metal ores that may contain arsenic	Local exhaust ventilation, personal protective equipment
During cleaning of metal equipment, electroplating of metals, metallic pickling, soldering and etching, photo-duplication, and use of photographic emulsions	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

If arsine is leaked, the following steps should be taken:

1. Stop the flow of arsine gas. If the source of the leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to an area with local exhaust ventilation and repair the leak or allow the cylinder to empty.
2. Ventilate area of leak.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are done in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning.

The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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* Only NIOSH/MSHA-approved equipment should be used.

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POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about asbestos for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for various forms of asbestos: (1) Asbestos (mixed forms);
(2) Chrysotile;
(3) Amosite;
(4) Crocidolite;
(5) Tremolite;
(6) Anthophyllite;
(7) Actinolite.
If unspecified, data apply to all forms.

• **Composition:** (1) Not Available;
(2) 3MgO-2SiO_2-2H2O;
(3) (FeMg)SiO_3;
(4) $NaFe(SiO_3)_2$-$FeSiO_3$-H_2O;
(5) $Ca_2Mg_5Si_8O_{22}(OH)_2$;
(6) $(MgFe)_7Si_8O_{22}(OH)_2$;
(7) CaO-3(MgFe)O-4SiO_2

• **Synonyms:** (1) Asbestos fiber, serpentine, amphibole;
(2) Canadian chrysotile, white asbestos, serpentine;
(3) Brown asbestos, fibrous grunerite;
(4) Blue asbestos;
(5) Fibrous tremolite;
(6) Azbolen asbestos;
(7) Not available

• **Identifiers:** (1) CAS 1332-21-4; RTECS CI6475000; DOT 2212 (blue) 2590 (white);
(2) CAS 12001-29-5; RTECS CI6478500; DOT 2590;
(3) CAS 12172-73-5; RTECS CI6477000; DOT Not assigned;
(4) CAS 12001-28-4, RTECS CI6479000; DOT 2212;
(5) CAS 14567-73-8; RTECS CI6560000; DOT Not assigned;
(6) CAS 17068-78-9; RTECS CI6478000; DOT Not assigned;
(7) CAS 13768-00-8; RTECS CI6476000; DOT Not assigned

• **Appearance and odor:** A fiber or filament, asbestos may have a "fluffy" appearance. Colors may vary from white, gray, blue, brown, green or yellow. Positive identification requires microscopic examination.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: (2) 277.13; (5) 185.03
2. Specific gravity (water = 1): 2.5-3.0
3. Noncombustible solid

• **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

Only asbestos fibers greater than 5 micrometers (μ)m in length are considered for the following exposure limits. The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for asbestos is 0.2 fiber per cubic centimeter (cc) of air as a time-weighted average (TWA) concentration over an 8-hour workshift with an action level of 0.1 fiber/cc as an hour TWA. The National Institute for Occupational Safety and Health (NIOSH) recommends that asbestos be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.1 fiber/cc (in 40-liter air sample) as a TWA concentration for up to an 8-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated asbestos as an Al substance (suspected human carcinogen, with an assigned threshold limit value/ TLV®) of 2 fibers/cc for chrysotile, 0.5 fiber/cc for amosite, 0.2 fiber/cc for crocidolite, and 2 fibers/cc for other forms, as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

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Public Health Service Centers for Disease Control
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Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for asbestos

	Exposure limits mg/m³*
OSHA PEL TWA	0.2
Action level	0.1
NIOSH REL TWA (Ca)†	0.1
ACGIH TLV® TWA (A1a)§	
Chrysotile	2.0
Amosite	0.5
Crocidolite	0.2
Other forms	2.0

* Fibers greater than 5 μm in length.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ (A1a): Human carcinogen with an assigned TLV®.

HEALTH HAZARD INFORMATION

• Routes of exposure

Asbestos may cause adverse health effects following exposure via inhalation or ingestion.

• Summary of toxicology

1. *Effects on animals:* Single intrapleural injections of asbestos in rats, rabbits, and hamsters produced mesothelioma (cancer of the chest or abdominal linings). In rats, chronic inhalation or oral administration of asbestos produced cancers of the lungs, stomach, kidneys, liver, or mammary glands. All forms of asbestos were found to be carcinogenic in treated animals.
2. *Effects on humans:* Exposure to asbestos has been found to significantly increase the risks of contracting asbestosis, lung cancer, and mesothelioma.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to asbestos can cause shortness of breath, chest or abdominal pain, and irritation of the skin and mucous membranes.
2. *Long-term (chronic):* Exposure to asbestos can cause reduced pulmonary function, breathing difficulty, dry cough, broadening and thickening of the ends of the fingers, and bluish discoloration of the skin and mucous membranes.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, and morbidity and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to asbestos, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to asbestos at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include cigarette smoking, preexisting asbestos-related disease, and significant breathing impairment due to preexisting chronic lung diseases. In addition to the medical interview and physical examination, the means to identify these conditions may include the methods recommended by NIOSH and ATS.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to asbestos. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory system as compared to the baseline status of the individual worker or to the expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, tests of lung function, and chest X-rays.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because

occupational exposure to asbestos may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

Delayed-onset SHE's include: Scarring of the lungs (asbestosis) and its lining (pleural fibrosis) and cancer of the lungs (bronchogenic lung cancer) and its lining (mesothelioma).

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to asbestos should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis for airborne asbestos may be performed by collecting asbestos fibers with membrane filters and analyzing by phase contrast microscopy. A detailed sampling and analytical method for asbestos may be found in the *NIOSH Manual of Analytical Methods* (method number 7400).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with asbestos.

SANITATION

Clothing which is contaminated with asbestos should be removed at the end of the work period and placed in nonreusable, impermeable containers for storage, transport, and disposal until it can be discarded or until provision is made for the removal of asbestos from the clothing. These containers should be marked "Asbestos-Contaminated Clothing" in easy-to-read letters. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of asbestos's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with asbestos should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle asbestos should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to asbestos may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for asbestos

Operations	Controls
During asbestos removal	Process enclosure, wet process (when possible), personal protective equipment
During the production of asbestos or the manufacture of products containing asbestos	Process enclosure, local exhaust ventilation, wet process (when possible), personal protective equipment
During the demolition of buildings	Water spray, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to asbestos, an eye wash fountain should be provided within the immediate work area for emergency use.

If asbestos gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this substance.

• **Skin exposure**

If asbestos gets on the skin, wash it immediately with soap and water.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If asbestos is spilled or leaked, the following steps should be taken:

Asbestos dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for asbestos

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ATRAZINE

INTRODUCTION

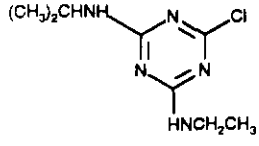
This guideline summarizes pertinent information about atrazine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8H_{14}ClN_5$

- **Structure**



- **Synonyms**

Aatrex; Atranex; Atratol A; Atred; 2-chloro-4-ethylamino-6-isopropylamino-s-triazine; 6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine; Crisatrina; Fenamin; Gesaprim; Griffex; Hungazin; Inakor; Primatol; Radazin; Shell Atrazine Herbicide; Strazine; Triazine A1294; Vectral; Weedex A; Zeazine

- **Identifiers**

1. CAS No.: 1912-24-9
2. RTECS No.: XY5600000
3. DOT UN: 2763 53
4. DOT label: Poison

- **Appearance and odor**

Atrazine is an odorless, nonflammable, colorless or white, crystalline solid. This chemical is a triazine herbicide that is available commercially as a wettable powder or a liquid emulsion and is often combined with other herbicides.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 215.72
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 1.19 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 171° to 174°C (339.8° to 345.2°F)
6. Vapor pressure at 20°C (68°F): 0.0000003 mm Hg
7. Solubility: Slightly soluble in water; soluble in diethyl ether, methanol, chloroform, dimethyl sulfoxide, ethyl acetate, and n-pentane
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat. Atrazine is very stable; it has a shelf life of several years but is slightly sensitive to natural light and extreme temperatures.
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, hydrogen chloride, and oxides of nitrogen) may be released in a fire involving atrazine.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to atrazine; this substance is not flammable.

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Occupational Safety and Health Administration

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving atrazine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving atrazine. Firefighters' protective clothing may not provide protection against permeation by atrazine.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for atrazine is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned atrazine a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The OSHA and NIOSH limits are based on the risk of neuropathic and metabolic effects associated with exposure to atrazine. The ACGIH limit is based on the acute effects of exposure to atrazine.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to atrazine can occur through inhalation, ingestion, or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Atrazine is an irritant of the eyes and skin in animals; at high doses, it causes nervous system effects. Eyelid edema and conjunctivitis occurred after application of atrazine to the eyes of guinea pigs, cats, and rabbits [NLM 1991]. In separate studies, it also induced severe eye irritation when applied to the eyes of rabbits [NIOSH 1991] and caused mild irritation when applied to their skin [NIOSH 1991]. The dermal LD_{50} in rabbits is 7,500 mg/kg [NIOSH 1991]. When applied to the skin of rats, atrazine caused marked erythema but no systemic toxicity [Hayes 1982]. Groups of rats that inhaled atrazine aerosol concentrations (80% wettable powder) ranging from 1,800 to 4,900 mg/m^3 for 1 hr developed no signs or symptoms of toxicity [NLM 1991]. The LC_{50} in rats is 5,200 mg/m^3 for 4 hr [NIOSH 1991]. The oral LD_{50} in mice is 1,750 mg/kg [NLM 1991]. The oral LD_{50} in rats ranges from 672 mg/kg [NIOSH 1991] to 3,080 mg/kg [NLM 1991]. Oral administration of a large amount of atrazine to rats caused them to develop muscular weakness, hypoactivity, ptosis, dyspnea, and prostration [NLM 1991]. The effects induced in rats following oral administration of the LD_{100} (3,000 mg/kg) included depression, reduced respiratory rate, motor incoordination, clonic/tonic convulsions, hypothermia, and central nervous system lesions (undefined) [NLM 1991]. Rats receiving atrazine by gavage (100, 200, or 400 mg/kg per day for 7 or 14 days) showed a dose-dependent increase in liver weight and histopathological changes in the liver [NLM 1991]. Forty percent of rats that received 20 mg/kg per day for 6 months developed bronchitis, peribronchitis, respiratory distress, pericapillary edema, and dystrophy of the brain before death [NLM 1991]. In addition, rats receiving either 10 or 50 mg/kg per day for 6 months by gavage had inhibited growth rates, leukopenia, and disturbances in vitamin metabolism [NLM 1991]. Atrazine is embryotoxic at high, maternally toxic oral doses [NLM 1991]. Some carcinogenicity bioassays with atrazine have been positive [NLM 1991]. Atrazine is mutagenic in several mammalian test systems, including human fibroblasts [NIOSH 1991; NLM 1991]. Oral administration of atrazine for up to 2 yr did not induce cancers in treated mice or rats [ACGIH 1991a; NLM 1991].

2. *Effects on Humans*: In humans, atrazine causes skin irritation [NLM 1991]. No toxicity resulted when a child ingested 800 mg or when an adult ingested 4 mg/kg [NLM 1991]. A farmer who sprayed an atrazine formulation reported a case of severe contact dermatitis; he had red, swollen hands and bloody blisters between the fingers. A patch test later showed the farmer to be sensitized to atrazine [Hayes 1982]. Atrazine may also be mutagenic in humans: lymphocytes of agricultural workers exposed to atrazine showed a statistically significant increase in the incidence of chromosomal aberrations during the spraying season [EPA 1987]. Some evidence suggests that exposure to triazine herbicides increases the risk of ovarian cancer in exposed women [NLM 1991].

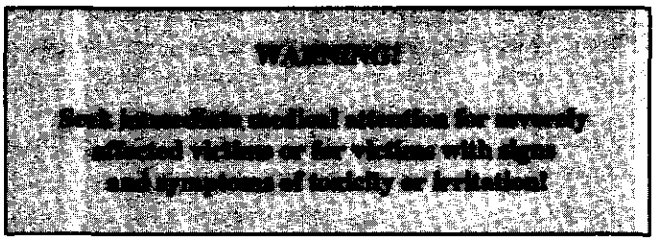
• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to atrazine can cause severe irritation of the eyes and mild skin irritation. Mus-

cular weakness, hypoactivity, ptosis, dyspnea, prostration, depression, reduced respiratory rate, motor incoordination, clonic/tonic convulsions, and hypothermia have also been reported in atrazine-exposed animals.

2. *Chronic exposure*: Chronic exposure of animals to atrazine has produced tissue irritation and inhibited growth rates.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of atrazine. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If particulates, vapors, mists, or aerosols of atrazine are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if atrazine or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of seizures.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of atrazine may result in worker exposures to this substance:

—Use in the manufacture, formulation, or application of herbicides

—Use as a selective herbicide for control of broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, asparagus, tomato, and potato fields; macadamia orchards; conifer reforestation sites; Christmas tree plantations; and grass seed fields

—Use as a nonselective herbicide (at higher concentrations) for industrial and commercial noncropped sites such as railroads, storage yards, and highways

—Use as an algicide in lakes and ponds

—Use as a turf grass sod herbicide

The following methods are effective in controlling worker exposures to atrazine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease.

The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to atrazine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and on a history of skin allergies.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to atrazine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to atrazine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of atrazine on the skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for atrazine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne atrazine is determined by using a glass fiber filter. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 240 liters is collected. Analysis is conducted by high-pressure liquid chromatography using an ultraviolet detector. This method is described in the OSHA Computerized Information System [OSHA 1990] and in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If atrazine contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with atrazine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of atrazine, particularly its potential for causing skin irritation.

A worker who handles atrazine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where atrazine or a solution containing atrazine is handled, processed, or stored.

STORAGE

Atrazine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of atrazine should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly

contained atrazine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving atrazine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For small dry spills, use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the atrazine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Atrazine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of atrazine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of the SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of atrazine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although atrazine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of atrazine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For

additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Gloves and protective clothing should be worn to prevent skin contact with atrazine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to permeation by atrazine formulations. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to atrazine.

If atrazine is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which atrazine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with atrazine. Contact lenses should not be worn if the potential exists for atrazine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AZINPHOS-METHYL

INTRODUCTION

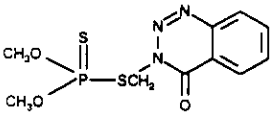
This guideline summarizes pertinent information about azinphos-methyl for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{12}N_3O_3PS_2$

- **Structure**



- **Synonyms**

Guthion; methyl guthion; benzotriazine derivative of methyl dithiophosphate; benzotriazine-dithiophosphoric acid, dimethoxy ester; O-O-dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl-methyl] phosphoro-dithioate; Bay 9027; Bayer 9027; Carfene; Cotnion methyl; Gusathion

- **Identifiers**

1. CAS No.: 86-50-0
2. RTECS No.: TE1925000
3. DOT UN: 2783 55
4. DOT label: Poison

- **Appearance and odor**

Azinphos-methyl is an organophosphorus pesticide. The technical product is a brown waxy solid; no data are available regarding the odor of this substance.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 317.34
2. Boiling point (at 760 mm Hg): Decomposes at temperatures above 200°C (392°F)
3. Specific gravity (water = 1): 1.44 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 73° to 74°C (163.4° to 165.2°F)
6. Vapor pressure at 20°C (68°F): 0.00038 mm Hg
7. Solubility: Slightly soluble in water; soluble in methanol, ethanol, propylene glycol, xylene, and other organic solvents
8. Evaporation rate: Negligible

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or flame.
2. Incompatibilities: Fires and explosions may result from contact of azinphos-methyl with strong oxidizers.
3. Hazardous decomposition products: Toxic gases and dusts (such as oxides of nitrogen, phosphorus, and sulfur) may be released when azinphos-methyl is heated to decomposition.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to azinphos-methyl; this substance may burn, but it does not ignite readily.

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or standard foam to fight small fires involving

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

azinphos-methyl; use water spray, fog, or standard foam to fight large fires involving this substance.

Fires involving azinphos-methyl should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of azinphos-methyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving azinphos-methyl. Chemical protective clothing that is specifically recommended for azinphos-methyl may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by azinphos-methyl.

EXPOSURE LIMITS

• OSHA PEL

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for azinphos-methyl is 0.2 mg/m^3 of air as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.2 mg/m^3 as an 8-hr TWA with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned azinphos-methyl a threshold limit value (TLV) of 0.2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek; the TLV also bears a "Skin" notation [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of anticholinesterase effects associated with exposure to azinphos-methyl.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to azinphos-methyl can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Azinphos-methyl is a cholinesterase inhibitor in animals that is capable of inducing death from respiratory arrest. Significant dermal absorption can occur in animals. The dermal LD_{50} is about 65 mg/kg in mice and 220 mg/kg in rats [NIOSH 1991]. Among rats that inhaled an aerosol of technical grade product containing 72% to 73% azinphos-methyl, the 1-hr LC_{50} was approximately 75 mg/m^3 (69 mg/m^3 for males and 79 mg/m^3 for females). The signs and symptoms of toxic cholinesterase inhibition included salivation, lacrimation, exophthalmos, defecation, urination, and muscle fasciculations before respiratory failure and death [NIOSH 1991; SRI 1978]. The oral LD_{50} was 15 mg/kg in mice and 7 mg/kg in rats [NIOSH 1991]. Rats that inhaled azinphos-methyl at 4.72 mg/m^3 for 12 weeks (6 hr/day, 5 days/week) showed a significant reduction in erythrocyte and plasma cholinesterase activity [Proctor et al. 1988]. Rats tolerated a dietary concentration of 5 ppm for 60 days without cholinesterase inhibition; at 20 ppm for 60 days, however, brain and red blood cell cholinesterase levels were inhibited by as much as 30% [ACGIH 1991a]. When azinphos-methyl was administered to pregnant mice and rats, it caused no adverse developmental effects in the offspring [NIOSH 1991; NLM 1991]. A National Cancer Institute study provided equivocal evidence that oral dosing of male rats with azinphos-methyl causes cancer of the thyroid and pancreas; this substance was not shown to be carcinogenic in female rats or in male or female mice [NCI 1978].

2. *Effects on Humans*: Azinphos-methyl is a cholinesterase inhibitor in humans. Eight workers engaged in the formulation of a wettable azinphos-methyl powder were exposed to concentrations as high as 9.6 mg/m^3; blood serum levels in some workers were depressed to 78% of their pre-exposure baseline cholinesterase levels [Proctor et al. 1988]. In a group of male agricultural workers working in a field that had been treated with azinphos-methyl, the mean red blood cell cholinesterase activity was significantly below that of workers engaged in an untreated field [NLM 1991]. Volunteers ingesting 4 to 20 mg azinphos-methyl/day for 30 days did not show a drop in cholinesterase levels [ACGIH 1991a].

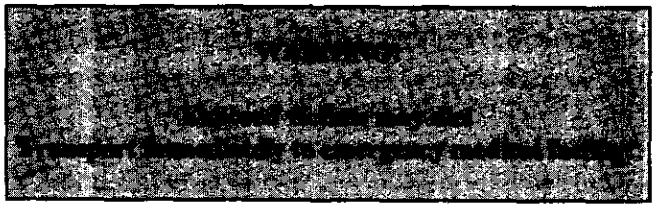
• Signs and symptoms of exposure

1. *Acute exposure*: The following signs and symptoms of acute exposure to azinphos-methyl vary with the route of entry and the degree of exposure [NLM 1991]. Effects associated with inhalation exposure include a feeling of

tightness in the chest, wheezing, bronchoconstriction, excessive bronchial secretion, laryngeal spasms, excessive salivation, cyanosis, miosis, pain in and between the eyes, blurring of distant vision, tearing, rhinorrhea, and frontal headache. Within 15 to 120 min of ingestion, gastrointestinal effects appear—anorexia, nausea, vomiting, abdominal cramps, and diarrhea. After skin absorption, sweating and muscle twitching occur in the area of skin contact. If overexposure by any route is severe, signs and symptoms include muscular weakness, involuntary twitching, and eventually paralysis. The most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. Blood pressure may fall, and cardiac irregularities (including complete heart block) may occur; these effects are sometimes reversible if adequate pulmonary ventilation is established. Unless the exposure is lethal, complete symptomatic recovery usually occurs within 1 week; however, increased susceptibility to the effects of anticholinesterase agents usually persists for several weeks after exposure.

2. *Chronic exposure*: Repeated exposure to azinphos-methyl at concentrations below those that will cause symptoms after a single exposure can cause the same signs and symptoms as acute exposure.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Azinphos-methyl can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of azinphos-methyl are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose to remove particulates or residues from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if azinphos-methyl or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations involve azinphos-methyl and may result in worker exposures to this substance:

—Manufacture, formulation, and application of azinphos-methyl as an insecticide and acaricide on field crops, fruits, vegetables, cotton, tobacco, nuts, sugar cane, soybeans, ornamentals, grasses, and trees

—Use of azinphos-methyl as an additive in the food and drinking water of animals

The following methods are effective in controlling worker exposures to azinphos-methyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to azinphos-methyl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood. A baseline red blood cell acetylcholinesterase level should be established for each potentially exposed worker.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to azinphos-methyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with decreases in blood cholinesterase activity.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to azinphos-methyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of azinphos-methyl on blood cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Red blood cell cholinesterase activity can be measured to monitor both acute and chronic exposure to azinphos-methyl. A worker should be removed from exposure if his or her erythrocyte cholinesterase level drops to or below 40% of the pre-exposure baseline value for that individual; he or she should not be allowed to return to work until this level has again reached 80% of the pre-exposure baseline level.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Neither NIOSH nor OSHA has a validated method for sampling azinphos-methyl in the workplace. However, the following secondary analytical method, which has not been validated, is available.

A worker's exposure to airborne azinphos-methyl is determined by using a specially designed tube called an OSHA versatile sampler (OVS-2) containing XAD-2 resin (270/140-mg sections, 20/60 mesh) and a glass fiber filter. Samples are collected at a recommended flow rate of 1 liter/min until a recommended air volume of 480 liters is collected. The sample is desorbed with toluene. Analysis is conducted by gas chromatography using a flame photometric detector and an OV-1 column at 175°C (347°F). The limit

of detection for this procedure is 5 μg/sample. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

Because azinphos-methyl can be deadly if absorbed through the skin, an exposed worker should remove any contaminated clothing immediately and flush the affected areas with copious amounts of water for 15 min; the worker should then wash thoroughly with soap and water. At the end of the day, workers who handle azinphos-methyl or liquid containing azinphos-methyl should use soap and water to wash any areas of the body that may have contacted this pesticide, even if none is detected on the skin.

Clothing and shoes contaminated with azinphos-methyl should be removed immediately; speed in removing these articles is essential. Persons laundering contaminated clothing should be informed of the hazardous properties of azinphos-methyl, particularly its potential for being absorbed through the skin.

A worker who handles azinphos-methyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where azinphos-methyl or a solution containing it is handled, processed, or stored.

STORAGE

Azinphos-methyl should be stored in a cool, dry, well-ventilated area in tightly sealed original containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of azinphos-methyl should be protected from physical damage and should be separated from oxidizers, heat, sparks, and open flame. Azinphos-methyl should never be stored near any type of food. Because containers that formerly contained azinphos-methyl may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving azinphos-methyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the atmosphere to reduce the concentration.
4. Use water spray to reduce vapors.
5. For dry spills (azinphos-methyl in solid form), use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
6. Absorb small liquid spills (azinphos-methyl formulations) with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the azinphos-methyl for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 10,000 lb or more of azinphos-methyl onsite must comply with EPA's emergency planning requirements [40 CFR 355.30]. (The employer must comply with these requirements if azinphos-methyl is in the form of a finely divided powder or is handled in solution or in molten form, and if 10 lb or more is present at the facility.)

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for azinphos-methyl is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of azinphos-methyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although azinphos-methyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of azinphos-methyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with azinphos-methyl. Gloves, overalls, and boots should be worn when handling azinphos-methyl or any organophosphorus pesticide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by azinphos-methyl and may provide protection for periods greater than 8 hr: neoprene and nitrile rubber. Natural rubber and polyvinyl chloride have demonstrated questionable resistance to permeation by azinphos-methyl.

If azinphos-methyl is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which azinphos-methyl might contact the eyes (e.g., through dust particles, mists, or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with azinphos-methyl. Contact lenses should not be worn if the potential exists for azinphos-methyl exposure.

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Occupational Health Guideline for Soluble Barium Compounds (as Barium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble barium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Barium nitrate

- Formula: $Ba(NO_3)_2$
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium oxide

- Formula: BaO
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium carbonate

- Formula: $BaCO_3$
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium chloride

- Formula: $BaCl_2$
- Synonyms: None
- Appearance and odor: Odorless white solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble barium compounds is 0.5 milligram of soluble barium compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble barium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Soluble barium compounds may cause local irritation of the eyes, nose, throat, bronchial tubes, and skin. Soluble barium compounds may also cause severe stomach pains, slow pulse rate, irregular heart beat, ringing of the ears, dizziness, convulsions, and muscle spasms. Death may occur.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble barium compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble barium compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the heart, lungs, and nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Soluble barium compounds cause human lung damage. Surveillance of the lungs is indicated.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

—FVC and FEV (1 sec): Soluble barium compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Electrocardiogram: Barium compounds may cause cardiac arrhythmias and may have a direct effect on the cardiac muscle. Periodic surveillance of the heart is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

• **Summary of toxicology**

Soluble barium salts cause severe gastroenteritis and systemic effects by ingestion. Intravenous injection of barium compounds in animals causes a strong, prolonged stimulation of muscle resulting in hyperperistalsis, bladder contraction, vasoconstriction, and irregular contraction of the heart followed by arrest in systole. Animals also exhibit stimulation of the central nervous system followed by paralysis. Ingestion of barium carbonate by humans causes gastroenteritis, muscular paralysis, slow pulse rate, extrasystoles, and hypokalemia. Heavy industrial exposure to dusts of barium sulfate or barium oxides may produce a benign pneumoconiosis, termed baritosis. It results in no impairment of ventilatory function, although signs of mild bronchial irritation may occur. Characteristic x-ray changes are those of small, dense, circumscribed nodules evenly distributed throughout the lung fields, reflecting the radio-opacity of the barium dust. Bronchial irritation has been reported from the inhalation of barium carbonate dust. Barium hydroxide and barium oxide are strongly alkaline in aqueous solution, causing severe burns of the eye and irritation of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Barium nitrate**

1. Molecular weight: 261.4
2. Boiling point (760 mm Hg): Greater than 592 C (greater than 1098 F) (decomposes)
3. Specific gravity (water = 1): 3.24
4. Vapor density (air = 1 at boiling point of barium nitrate): Not applicable
5. Melting point: 592 C (1098 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 9.2
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium oxide**

1. Molecular weight: 153.3
2. Boiling point (760 mm Hg): 2000 C (3632 F)
3. Specific gravity (water = 1): 5.72
4. Vapor density (air = 1 at boiling point of barium oxide): Not applicable
5. Melting point: 1921 C (3490 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium carbonate**

1. Molecular weight: 197.3
2. Boiling point (760 mm Hg): 1300 C (2372 F) (decomposes)
3. Specific gravity (water = 1): 4.25
4. Vapor density (air = 1 at boiling point of barium carbonate): Not applicable
5. Melting point: Decomposes at 1300 C (2372 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0022
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium chloride**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 1560 C (2840 F)
3. Specific gravity (water = 1): 3.86
4. Vapor density (air = 1 at boiling point of barium chloride): Not applicable
5. Melting point: 963 C (1765 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 36
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: For barium nitrate, elevated temperatures may cause melting and decomposition; for the other compounds, none hazardous.
2. Incompatibilities: Contact of barium oxide with water, carbon dioxide, or hydrogen sulfide may cause fires and explosions. Contact of barium carbonate with acids causes formation of carbon dioxide gas that may cause suffocation in enclosed spaces. Contact of barium nitrate with organic matter and combustible materials may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving barium nitrate.
4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: For barium nitrate, data not available; for the the other compounds, not applicable.
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Large amounts of water should be used on adjacent fires.

• **Warning properties**

According to Grant, barium chloride causes "considerable iritis, which subsides in a few days" when "tested

in neutral 0.08 to 0.1 M solution on rabbit eyes by injection into the cornea or by dropping for 10 minutes on the eye after the corneal epithelium was removed to facilitate penetration." Grant states that "both the oxide and hydroxide are capable of causing severe alkali burns of the eye, similar to those produced by calcium hydroxide."

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by leaching in hot water, solution of sample in acid, and analysis in an atomic absorption spectrophotometer. An analytical method for soluble barium compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with barium carbonate, barium chloride, barium nitrate, or liquids containing these compounds.

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with barium oxide or liquids containing barium oxide, where skin contact may occur.

• If employees' clothing has had any possibility of being contaminated with barium carbonate, barium chloride, barium nitrate, barium oxide, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with barium carbonate, barium chloride, barium nitrate, or barium oxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.

• Where exposure of an employee's body to barium oxide or liquids containing barium oxide may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with barium carbonate, barium chloride, barium nitrate, or barium oxide should be removed promptly and not reworn until the contaminant is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of barium oxide or liquids containing barium oxide contacting the eyes.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where barium carbonate, barium chloride, barium nitrate, or liquids containing these compounds may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to barium oxide or liquids containing barium oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Workers subject to skin contact with barium oxide or liquids containing barium oxide should wash any areas of the body which may have contacted barium oxide at the end of each work day.

• Skin that becomes contaminated with barium carbonate, barium chloride, or barium nitrate should be promptly washed or showered to remove any contaminant. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

• Skin that becomes contaminated with barium oxide should be promptly washed or showered to remove any barium oxide from the skin after all obvious amounts of barium oxide have been removed by other means (e.g., by use of oil or vaseline). Employees who are being burned by barium oxide should immediately utilize quick drenching facilities without first removing barium oxide by other means.

• Eating and smoking should not be permitted in areas where solid barium carbonate, barium chloride, barium nitrate, or barium oxide, or liquids containing these compounds are handled, processed, or stored.

• Employees who handle barium carbonate, barium chloride, barium nitrate, barium oxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble barium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Manufacture and distribution of soluble barium compounds	Process enclosure; local exhaust ventilation
Use in manufacture of pressed and blown glasssware and flint and crown optical glass; manufacture of ceramic products; use in electronics industry in manufacture of magnets, vacuum tubes, cathodes, x-ray fluorescent screens, TV picture tubes, and dry cell depolarizers	Process enclosure; local exhaust ventilation
Use in manufacture of photographic papers, dyes, and chemicals	Process enclosure; local exhaust ventilation
Use as pesticides, rodenticides, and disinfectants; use in manufacture of explosives, matches, and pyrotechnics as igniter compositions and fireworks	Process enclosure; local exhaust ventilation
Use as an additive in manufacture of grease, and manufacture of lubricating oils; use in refining of vegetable and animal oils	Process enclosure; local exhaust ventilation
Use in case-hardening of steel in metallurgy; in welding aluminum; in electroplating; and in aluminum and sodium refining	Process enclosure; local exhaust ventilation
Use in water treatment and boiler compounds for softening water; use as catalysts, analytical reagents, and purifying agents	Process enclosure; local exhaust ventilation
Use for treatment of textiles, leather, and rubber; use in manufacture of paper and cellulose as a bleaching agent; use in manufacture of pigments, colors, and lakes	Process enclosure; local exhaust ventilation
Use as a depilatory in processing of hides; as a fire-proof and extinguishing agent; in embalming; in sugar refining; in gas and solvent drying; in marble substitutes; in valve manufacture; and as a smoke suppressant in diesel fuels	Process enclosure; local exhaust ventilation
Use in manufacture of pigments, paints, enamels, and printing inks	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If solutions of barium compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

• **Skin Exposure**

If solutions of barium compounds get on the skin, immediately flush the contaminated skin with water. If solutions of barium compounds soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of soluble barium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When soluble barium compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If soluble barium compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquids containing soluble barium compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Soluble barium compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SOLUBLE BARIUM COMPOUNDS (AS BARIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate Concentration	
2.5 mg/m³ or less	Any dust and mist respirator, except single-use.**
5 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying respirator with a high efficiency particulate filter.
Greater than 250 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BARIUM SULFATE

INTRODUCTION

This guideline summarizes pertinent information about barium sulfate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$BaSO_4$

- **Synonyms**

Actybaryte; artificial barite; artificial heavy spar; bakontal; baridol; barite; barosperse; barotrast; baryta white; barytes; bayrites; citobaryum; colonatrast; finemeal; liquibarine; macropaque; neobar; oratrast; permanent white; precipitated barium sulphate; raybar; redi-flow; solbar; sulfuric acid, barium salt (1:1); supramike; travad; unibaryt

- **Identifiers**

1. CAS No.: 7727-43-7
2. RTECS No.: CR0600000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Barium sulfate is a heavy, noncombustible, white or yellowish, odorless powder or crystalline solid. It occurs naturally as the mineral barite and can also be manufactured. Barium sulfate is available in several commercial grades, including technical, dry, pulp, bleached, ground, floated, natural, pharmaceutical, and X-ray.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 233.42
2. Boiling point (760 mm Hg): Not applicable
3. *Specific gravity (water = 1):* 4.25 to 4.50 at 20°C (68°F)
4. Vapor density: Not applicable.
5. Melting point: 1,580°C (2,876°F); decomposes above 1,600°C (2,912°F)
6. Vapor pressure at 20°C (68°F): Not applicable
7. Solubility: Almost insoluble in water, dilute acids, or alcohol; soluble in hot concentrated sulfuric acid
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Explosions may result from contact of barium sulfate with aluminum in the presence of heat.
3. Hazardous decomposition products: Toxic gases and particulates (such as sulfur oxides or barium fumes) may be released in a fire involving barium sulfate.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to barium sulfate; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving barium sulfate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of barium sulfate may

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explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Do not scatter this material. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving barium sulfate. Chemical protective clothing that is specifically recommended for barium sulfate may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by barium sulfate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for barium sulfate is 10 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr TWA concentrations [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned barium sulfate a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye, nose, and upper respiratory tract irritation and pneumoconiosis associated with exposure to barium sulfate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to barium sulfate can occur through inhalation and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Barium sulfate dust is a mechanical irritant. Rats exposed to a 40-mg/m^3 concentration of barium sulfate dust for 5 hr/day during a 2-month period did not show adverse effects [ACGIH 1991a]. In another study, rats inhaling barium sulfate dust (concentration not specified) developed a reversible pneumoconiosis without fibrosis [NLM 1991]. Intratracheal injection of radioactive barium sulfate caused bronchogenic carcinomas in rats [Clayton and Clayton 1981].

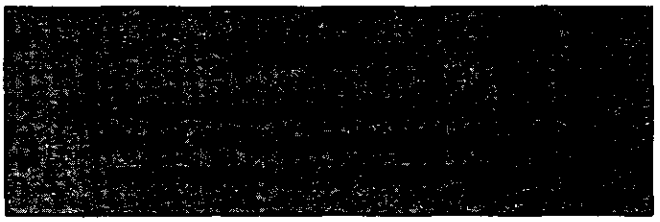
2. *Effects on Humans*: Inhalation of barium sulfate causes physical irritation and a benign pneumoconiosis (known as baritosis) in humans. In Italy, Germany, Czechoslovakia, and the United States, workers exposed to the fine dust of barium sulfate have developed a benign, noncollagenous form of pneumoconiosis that generally disappears when exposure ceases. Although chronic bronchial irritation occasionally persists after termination of exposure, no adverse effects on pulmonary function have been reported [Clayton and Clayton 1981; NLM 1991].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to barium sulfate can cause redness and itching of the eyes and nose and a scratchy throat. No other acute effects have been reported.

2. *Chronic exposure*: Chronic exposure to barium sulfate can cause radiographic evidence of disseminated, discrete nodular opacities in the lung fields; in most cases, these opacities disappear after cessation of exposure. Chronic bronchial irritation has been reported occasionally in baritotic workers.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Seek medical attention if signs and symptoms of toxicity develop, or take the following steps if a large amount of barium sulfate is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a fluid such as water.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve barium sulfate and may result in worker exposures to this substance:

—Mining, grinding, and bagging of barite and manufacture of barium sulfate

—Use of barium sulfate in oil-drilling muds, as a filler and delustrant for textiles, and as an expander in battery plate pastes

—Manufacture of lithopane, a white pigment

—Use of barium sulfate as a source of other barium compounds

—Manufacture of photographic papers, glass, ceramics, artificial ivory, cellophane, filler for rubber, linoleum, oil cloth, polymeric fibers and resins, and lithographic inks

—Use of barium sulfate as a diagnostic aid and X-ray contrast medium

—Use of barium sulfate as a watercolor pigment for colored paper and wallpaper, as an agent for modifying the colors of other pigments, and as an ingredient in the heavy concrete used for radiation shielding

The following methods are effective in controlling worker exposures to barium sulfate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to barium sulfate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to barium sulfate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to barium sulfate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of barium sulfate on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for barium sulfate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne barium sulfate is determined by using a tared, low-ash polyvinyl chloride (LAPVC) filter (5-micron) to measure both total dust and the respirable fraction (a 10-mm nylon cyclone must be used for collecting the respirable fraction). Samples are collected at a maximum flow rate of 2 liters/min (total dust) or 1.7 liters/min (respirable fraction) until a maximum air volume of 960 liters (total dust) or 816 liters (respirable fraction) is collected. Gravimetric analysis is conducted by weighing the filters. This method has a sampling and analytical error of 0.10 and is described in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985] and in the OSHA Computerized Information System (respirable fraction and total dust) [OSHA 1990]. A similar method is described in Method 500 (Nuisance dust, total) and Method 600 (Nuisance dust, respirable) of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If barium sulfate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with barium sulfate should be removed to prevent physical irritation of the skin.

A worker who handles barium sulfate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where barium sulfate is handled, processed, or stored.

STORAGE

Barium sulfate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of barium sulfate should be protected from physical damage and should be stored separately from aluminum, heat, sparks, and open flame. Because containers that formerly contained barium sulfate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving barium sulfate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.

5. For small, dry spills, use a clean shovel and place the material into a clean, dry, covered container; remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Barium sulfate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.30] to notify the National Response Center of an accidental release of barium sulfate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Facilities in SIC codes 20 to 39 who employ 10 or more workers and who manufacture more than 25,000 lb of barium compounds (including barium sulfate) per calendar year or who use more than 10,000 lb of barium compounds per calendar year are required to comply with EPA requirements in 40 CFR 372 that mandate the submission of Toxic Chemical Release Inventory Forms.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although barium sulfate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing more information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of barium sulfate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn if necessary to prevent skin contact with barium sulfate (gloves, boots, aprons, and gauntlets).

Safety glasses, goggles, or face shields should be worn during operations in which barium sulfate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with barium sulfate. Contact lenses should not be worn if the potential exists for barium sulfate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENOMYL

INTRODUCTION

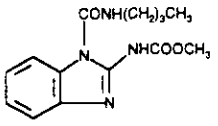
This guideline summarizes pertinent information about benomyl for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{14}H_{18}N_4O_3$

- **Structure**



- **Synonyms**

1-(Butylcarbamoyl)-2-benzimidazolecarbamic acid; methyl ester; 1-(butylcarbamoyl)-2-benzimidazol-methylcarbamat; 1-(n-butylcarbamoyl)-2-(methyoxy-carboxamido)-benzimidazol; carbamic acid; methyl 1-(butylcarbamoyl)-2-benzimidazole ester; Benlate; Arilate; BBC; Benlate 50; Benomyl 50W; BNM; Fundasol; Fungicide 1991; MBC; Tersan 1991

- **Identifiers**

1. CAS No.: 17804-35-2

2. RTECS No.: DD6475000

3. DOT UN: 2757 55 (carbamate pesticide, solid, not otherwise specified)

4. DOT label: Poison or St. Andrew's Cross (depending on quantity shipped)

- **Appearance and odor**

Benomyl is a noncombustible, white, crystalline solid that decomposes without melting. It has a faint, acrid odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 290.32

2. Boiling point (760 mm Hg): Not applicable

3. Specific gravity: Data not available

4. Vapor density: Data not available

5. Melting point: Decomposes without melting above 300°C (572°F)

6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

7. Solubility: Very slightly soluble in water; soluble in ethanol, heptane, xylene, acetone, dimethylformamide, and chloroform

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, water, strong acids, and strong alkalies can cause benomyl to decompose.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving benomyl.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating to benomyl; this substance is not combustible.

1. Flash point: Not applicable

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2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving benomyl.

EXPOSURE LIMITS

• **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benomyl is 10 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has no recommended exposure limit (REL) for benomyl [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned benomyl a threshold limit value (TLV) of 10 mg/m^3 (0.84 ppm) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• **Rationale for limits**

The OSHA limit is based on the risk of physical irritation, erythema, and potential reproductive effects associated with exposure to benomyl; the ACGIH limit is based on the low toxicity of this substance.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to benomyl can occur through inhalation and eye or skin contact.

• **Summary of toxicology**

1. *Effects on Animals*: Benomyl is a skin sensitizer, reproductive toxin, and teratogen in animals. When instilled into the eyes of rabbits, dry benomyl powder (50%) or 0.1 ml of a 10% benomyl solution produced only temporary, mild irritation of the conjunctiva [ACGIH 1991a]. When applied to the intact, shaved skin of guinea pigs, a benomyl concentration of 25% in a 50% wettable powder produced reddened skin in 1 of 10 animals; lower concentrations of benomyl did not cause skin irritation [ACGIH 1991a]. Benomyl caused mild to moderate skin sensitization in guinea pigs injected intradermally with benomyl and then challenged by topical application [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is greater than 10 g/kg [ACGIH 1991a]. The LC_{50} in rats is greater than 2,000 mg/m^3 for 4 hr. The oral LD_{50} in rats is 10 g/kg [NIOSH 1991]. Rats exposed to 100 mg/m^3 for 4 hr/day, 5 days/week for 3 weeks developed neither clinical or histopathological effects [NLM 1991]. Rats exposed to technical-grade benomyl at 10, 50, or 200 mg/m^3 for 6 hr/day, 5 days/week for 14 weeks had suppressed food consumptions and body weight gains at the highest level. Only the 50- and 200-mg/m^3 exposures induced any effect (a degeneration of the olfactory epithelium) after 45 days. Oral administration of benomyl (2,500 mg/kg in the diet) to rats for 90 days did not cause toxicity, but rats and dogs fed benomyl for 2 years exhibited a low order of toxicity (undefined) [NLM 1991].

A number of studies [Barnes et al. 1983; Carter et al. 1984; Ellis et al. 1987] have demonstrated benomyl's reproductive and teratogenic effects. Adult rats fed benomyl for 70 days showed significant depressions in sperm count and testicular weight and had lowered fertility indexes [Barnes et al. 1983]. Similar effects were elicited in rats given benomyl during or after puberty [Carter et al. 1984]. Rats intubated with benomyl doses ranging from 125 to 500 mg/kg per day during the first 20 days of pregnancy produced offspring with dose-related increases in the rates of skull and central nervous system anomalies [NLM 1991]. In addition, pregnant mice administered 1,100 mg/kg benomyl on days 7 to 17 of pregnancy had offspring with similar abnormalities [NIOSH 1991]. In another study, the offspring of rats given 31.2, 62.5, or 125 mg/kg by gavage on days 7 to 21 of gestation showed a dose-dependent increase in the incidence of craniocerebral and systemic malformations; an increase in fetal resorptions and late fetal deaths also occurred in the offspring of animals in the high-dose group [Ellis et al. 1987]. Although benomyl is mutagenic in bacterial test systems [NIOSH 1991], it did not induce cancer in either rats or dogs fed the compounds for two years [NLM 1991].

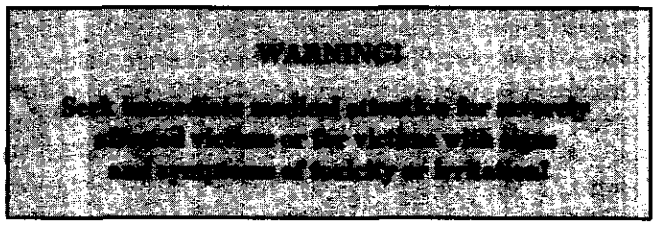
2. *Effects on Humans*: Benomyl is an irritant and skin sensitizer in humans. A recent U.S. study showed that two migrant workers in a group of farm workers with dermatitis had positive responses to 0.1% benomyl solutions in patch tests, indicating that they had become sensitized to this substance [Schuman and Dobson 1985]. A field study in Japanese farmers showed that 20% of women farmers had positive patch tests to benomyl as well as cross-sensitivities to other pesticides [Matsushita and Aoyama 1981]. Irritation, erythema, salivation, sweating, lassitude, reproductive effects, muscular incoordination, nausea, vomiting, abdominal cramps, angina pectoris, central nervous system depression, and cholinesterase inhibition have been reported [NLM 1991]. Benomyl is mutagenic in human in vitro test systems [NIOSH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to benomyl dust can cause irritation, erythema, salivation, sweating, lassitude, reproductive effects, muscular incoordination, nausea, vomiting, abdominal cramps, angina pectoris, central nervous system depression, and cholinesterase inhibition.

2. *Chronic exposure*: Chronic exposure to benomyl may cause skin sensitization with irritation, redness, and cholinesterase inhibition.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of benomyl. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of benomyl are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if benomyl or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve benomyl and may result in worker exposures to this substance:

—Manufacture and formulation of pesticides containing benomyl

—Use of benomyl as a systemic fungicide and ascaricide

—Use of benomyl in veterinary medicine as an anthelmintic

—Use of benomyl as an oxidizer in sewage treatment

The following methods are effective in controlling worker exposures to benomyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers

for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to benomyl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to benomyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies or other diseases of the skin. On the basis of effects seen in animals, men and women who plan to have children should be advised that they may be at increased risk of having a child with birth defects, and men should be advised that they may be at increased risk of experiencing adverse reproductive effects.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to benomyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of benomyl on the skin and the male reproductive system. Men and women who plan to have children should again be advised that they may be at increased risk of having a child with birth defects. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for benomyl.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne benomyl is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140-mg sections, 20/50 mesh). Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by high-performance liquid chromatography. This method is described in the OSHA Computerized Information System [OSHA 1989].

PERSONAL HYGIENE

If benomyl contacts the skin, workers should wash the affected areas with soap and water.

Clothing and shoes contaminated with benomyl should be removed, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of benomyl.

A worker who handles benomyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where benomyl or a solution containing benomyl is handled, processed, or stored.

STORAGE

Benomyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of benomyl should be protected

from physical damage and should be stored separately from strong acids, strong alkalies, heat, sparks, and open flame. Because containers that formerly contained benomyl may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving benomyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For dry spills, use a vacuum or a wet method to reduce dust dispersion and place the material into a clean, dry container; cover and remove the container from the spill area.
5. Absorb liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Benomyl is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of benomyl; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of benomyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although benomyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of benomyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For

additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with benomyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to benomyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to benomyl.

If benomyl is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which benomyl might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with benomyl. Contact lenses should not be worn if the potential exists for benomyl exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZENE

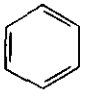
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about benzene for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_6H_6
- **Structure:**



- **Synonyms:** Benzol, benzole, benzolene, bicarburet of hydrogen, carbon oil, coal naphtha
- **Identifiers:** CAS 71-43-2; RTECS CY1400000; DOT 1114, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with an aromatic odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 78.12
2. Boiling point (at 760 mmHg): 80.1°C (176°F)
3. Specific gravity (water = 1): 0.88
4. Vapor density (air = 1 at boiling point of benzene): 2.7
5. Melting point: 5.5°C (42°F)
6. Vapor pressure at 20°C (68°F): 75 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.06
8. Evaporation rate (butyl acetate = 1): 5.1
9. Saturation concentration in air (approximate) at 25°C (77°F): 12.5% (125,000 ppm)
10. Ionization potential: 9.25 eV

- **Reactivity**

Incompatibilities: Benzene reacts with strong oxidizers including chlorine, oxygen, and bromine with iron.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving benzene.
3. Caution: Benzene will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -11.1°C (12°F) (closed cup)
2. Autoignition temperature: 498°C (928°F)
3. Flammable limits in air, % by volume: Lower, 1.4; upper, 7.1
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical extinguishants are effective. Water may be an ineffective extinguishant but may be used to cool fire-exposed containers.
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Unusual fire and explosion hazards: Benzene liquid is flammable, and its vapors can easily form explosive mixtures. Flashbacks may occur along a vapor trail.

- **Warning properties**

1. Odor threshold: 12 ppm
2. Eye irritation levels: 3,000 ppm for 0.5-1 hour
3. Other information: 3,000 ppm may irritate nose and respiratory tract.
4. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzene is 1 part of benzene per million parts of air (PPM) as a time-weighted average (TWA) concentration over an 8-hour workshift; the short-term exposure limit is 5 ppm in any 15-minute sampling period. The National Institute for Occupational Safety and Health (NIOSH) recommends that benzene be controlled and handled as a potential human carcinogen in the workplace and that exposure be reduced to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.1 ppm [0.32 milligrams of benzene per cubic meter of air (mg/m^3)] as an 8-hour TWA and 1 ppm (3.2 mg/m^3) as a ceiling in any 15-minute sampling period. The NIOSH REL is the lowest con-

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

centration detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated benzene as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 10 ppm (30 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for benzene

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	1	—
Short-term exposure limit (15 min)	5	—
NIOSH REL (Ca)* TWA	0.1	0.32
Ceiling (15 min)	1	3.2
ACGIH TLV® TWA (A2)†	10	30

* (Ca): NIOSH recommends treating as a potential human carcinogen.
†(A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure
Benzene may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology
1. *Effects on animals:* Acute inhalation of benzene by rats, mice, or rabbits caused narcosis, spontaneous heart contractions (ventricular fibrillation), and death due to respiratory paralysis. Subchronic inhalation of benzene by rats produced decreased white blood cell counts, decreased bone marrow cell activity, increased red blood cell activity, and cataracts. In rats, chronic inhalation or oral administration of benzene produced cancers of the liver, mouth, and Zymbal gland. Inhalation of benzene by pregnant rats caused retardation of fetal development and increased fetal mortality.
2. *Effects on humans:* Acute inhalation exposure of benzene has caused nerve inflammation (polyneuritis), central nervous system depression, and cardiac sensitization. Chronic exposure to benzene has produced anorexia and irreversible injury to the blood-forming organs; effects include aplastic anemia and leukemia.

• Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to benzene can cause dizziness, euphoria, giddiness, headache, nausea, staggering gait, weakness, drowsiness, respiratory irritation, pulmonary edema and pneumonia, gastrointestinal irritation, convulsions, and paralysis. Benzene can also cause irritation to the skin, eyes, and mucous membranes.
2. *Long-term (chronic):* Exposure to benzene can cause fatigue, nervousness, irritability, blurred vision, and labored breathing. Repeated skin contact can cause redness, blistering, and dry, scaly dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation
Prior to placing a worker in a job with a potential for exposure to benzene, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, and respiratory, nervous, and hematopoietic (blood-cell-forming) systems. The physician should obtain baseline values for the complete blood count and a stained differential count of all blood cell types. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to benzene at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindi-

cations to job placement, include a history of chronic skin disease, concurrent dermatitis, or mild non-hemolytic anemia (e.g., mild iron-deficiency anemia).

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to benzene. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, and respiratory, nervous, and hematopoietic (blood-cell-forming) systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination.**
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to benzene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**
1. Acute SHE's include: Acute myeloid leukemia and contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Decrease in the number (neutropenia) or absence (agranulocytosis) of certain white blood cells in the peripheral circulation and/or in the bone marrow (aplastic anemia) and cancer of the red blood cells (erythroleukemia).

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**
Measurements to determine worker exposure to benzene should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Ceiling concentration evaluation**
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of benzene. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**
Sampling and analysis may be performed by collecting benzene vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure benzene may also be used if available. A detailed sampling and analytical method for benzene may be found in the *NIOSH Manual of Analytical Methods* (method number 1500).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with benzene.

SANITATION

Clothing which is contaminated with benzene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of benzene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of benzene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with benzene should be promptly washed with soap and water.

Workers who handle benzene should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to benzene may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for benzene

Operations	Controls
During the manufacture and processing of benzene; during use as a raw material in the production of aromatic compounds and derivatives	Process enclosure, local exhaust ventilation, personal protective equipment
During the use of chemicals in which benzene may be an impurity (e.g., naphthas, toluene, xylene)	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture and use of motor fuel blends in which benzene is used as an ingredient; during use as an extracting solvent	Process enclosure (when possible), local exhaust ventilation, personal protective equipment, material substitution
During the preparation and use of paint and varnish removers, rubber cements, and lacquers	Process enclosure (when possible), local exhaust ventilation, personal protective equipment, material substitution

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**
Where there is any possibility of a worker's eyes being exposed to benzene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If benzene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**
Where there is any possibility of a worker's body being exposed to benzene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If benzene gets on the skin, wash it immediately with soap and water. If benzene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**
If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If benzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing benzene, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing benzene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing benzene may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for benzene

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZIDINE

INTRODUCTION

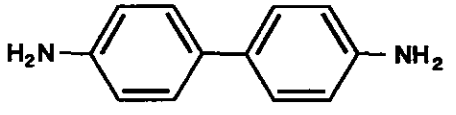
This guideline summarizes pertinent information about benzidine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{12}N_2$

- **Structure**



- **Synonyms**

1,1'-Biphenyl-4,4'-diamine, 4,4'-diaminobiphenyl, 4,4'-biphenyldiamine, 4,4'-bianiline, C.I. Azoic Diazo Component 112, Fast Corinth base B, p-diaminodiphenyl

- **Identifiers**

1. CAS No.: 92-87-5
2. RTECS No.: DC9625000
3. DOT UN: 1885 53
4. DOT label: Poison

- **Appearance and odor**

Benzidine is a white, gray-yellow, or slightly reddish crystalline solid or powder that has no odor. Benzidine is no longer manufactured commercially in the United States, although this substance is still used as an intermediate.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 184.2
2. Boiling point (at 760 mm Hg): 400°C (752°F)
3. Specific gravity (water = 1): 1.25 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of benzidine): 6.36
5. Melting point: 115°C (239°F)
6. Vapor pressure at 20°C (68°F): Quantitative data are not available, but vapor pressure is reported to be low.
7. Solubility: Slightly soluble in cold water; soluble in hot water, alcohol, and ether
8. Evaporation rate: Data not available

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- **Reactivity**

1. Conditions contributing to instability: None reported

2. Incompatibilities: Contact of benzidine with red fuming nitric acid may cause a fire.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, carbon monoxide, and benzidine vapors) may be released when benzidine is heated to decomposition.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for benzidine. Benzidine may burn, but it does not ignite readily.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to fight fires involving benzidine.

Fires involving benzidine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas. Containers of benzidine should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving benzidine. Structural firefighters' protective clothing may provide limited protection against fires involving benzidine.

EXPOSURE LIMITS

- **OSHA PEL**

Because benzidine is a recognized occupational carcinogen, the Occupational Safety and Health Administration (OSHA) standard for benzidine does not have a numerical permissible exposure limit (PEL); instead, the standard regulates the industrial use of benzidine by requiring implementation of stringent controls wherever benzidine or solid or liquid mixtures containing 0.1% or more benzidine by weight or volume are manufactured, processed, repackaged, released, handled, or stored. This standard is codified at 29 CFR 1910.1010.

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers benzidine a potential human carcinogen and recommends that the above standard [29 CFR 1910.1010] be followed [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated benzidine as an A1 substance (recognized human carcinogen). The ACGIH has also assigned benzidine a Skin notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The OSHA, ACGIH, and NIOSH limits are based on the risk of bladder and other cancer associated with exposure to benzidine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to benzidine can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Benzidine is a liver toxin and a potent carcinogen in experimental animals; in carcinogencity bioassays, this substance caused tumors of the liver, mammary gland, Zymbal gland, colon, and bladder in animals of several species. The oral LD_{50} in rats is 309 mg/kg [NIOSH 1993]. The oral LD_{50} in mice is 214 mg/kg [NIOSH 1993]. Benzidine has been tested for carcinogenicity in mice, rats, and hamsters by oral administration; in mice and rats by subcutaneous administration; and in rats by inhalation and by intraperitoneal administration. Except by

inhalation, benzidine caused increased incidences in tumors, both benign and malignant, in at least one sex of animal in all species tested. Oral administration in dogs also caused bladder cancers [IARC 1982]. With activation, benzidine is mutagenic in bacterial test systems [NIOSH 1993; IARC 1982]. The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence that benzidine is an animal carcinogen [IARC 1982].

2. *Effects on Humans:* Numerous case reports and epidemiological studies in workers from many countries, including the United States, have shown that benzidine is a potent carcinogen, causing papillomas and carcinomas of the urinary tract, and especially of the urinary bladder [IARC 1972; IARC 1982]. The latency period for benzidine tumors is 2 to 42 years, with an average latency of 16 years [Proctor et al. 1988]. In one U.S. dye manufacturing facility, bladder tumors developed in 36 workers who had been exposed to benzidine over a 45-year period (1930 to 1975) [IARC 1982]. In another group of 25 U.S. workers engaged in benzidine manufacture, 13 employees were found to have bladder tumors; all five of the workers in this group who had been exposed to benzidine for more than 15 years developed bladder tumors. Airborne benzidine concentrations at this plant were estimated to have ranged from 0.005 to 17.6 mg/m^3 [IARC 1982]. An increase in the number of sister chromatid exchanges has also been reported in workers exposed to benzidine [IARC 1982]. The International Agency for Research on Cancer has concluded that there is sufficient evidence that benzidine is a human carcinogen [IARC 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms for acute inhalation or dermal exposures have been reported. However, ingestion has caused nausea, vomiting, headache, mental confusion, dizziness, vertigo, methemoglobinemia, increase in the number of white blood cells, and Heinz bodies.

2. *Chronic exposure*: Chronic exposure to benzidine may cause blood in the urine (seen microscopically in early disease) and frequent and painful urination. The onset of bladder tumors may go undetected, and the disease may be in an advanced stage before any signs or symptoms appear. Despite aggressive treatment, tumors frequently recur.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of benzidine. Benzidine can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and thoroughly wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* If particulates or vapors, mists, or aerosols of benzidine are inhaled, move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if benzidine or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve benzidine and result in worker exposures to this substance:

—Use as an intermediate in the preparation of azo dyes and pigments

—Formerly used in forensic medicine to detect blood and other substances

—In declining use in security printing and as a stiffening agent in rubber compounding

—In declining use as a laboratory reagent

The only method that is effective in controlling worker exposures to benzidine is:

—Process enclosure

This substance should only be handled in closed systems.

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to benzidine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. The physician should consider whether there exist conditions associated with increased risk, including reduced immunological competence, treatment with steroids or cytotoxic agents, pregnancy, or cigarette smoking. The medical evaluation should concentrate on the function and integrity of the bladder, kidneys, liver, skin, and blood.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is potentially exposed to benzidine. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such condi-

tions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with bladder, kidney, liver, skin, and blood diseases.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to benzidine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of benzidine on the bladder, kidneys, liver, skin and blood. OSHA requires periodic examinations annually for workers potentially exposed to benzidine [29 CFR 1910.1010]. Suggested diagnostic tests include urinalysis every month (with particular attention to the presence of occult blood), urine cytology every 6 months, and cystoscopy as indicated. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urine benzidine levels may be useful in biological monitoring to assess exposure. Average urinary benzidine concentrations in workers exposed to benzidine concentrations in the range of 7 to 11 mg/m^3 are reported to be 9 mg benzidine per liter of urine (mg/l). In workers exposed to benzidine concentrations of 140 to 400 mg/m3, urinary benzidine levels reportedly range from 100 to 200 mg/l. As a carcinogen, benzidine or its metabolites should not be detectable in urine or other physiological fluids.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to benzidine may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne benzidine is determined by using a glass fiber filter coated with sulfuric acid. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 100 liters is collected. Immediately after sampling, the filter must be transferred to a vial containing 2 ml of deionized water. Analysis is conducted by gas chromatography using an electron capture detector. The limit of detection for this procedure is 4.1 mg/m^3. This method is described in Method 65 of the *OSHA Analytical Methods Manual* [OSHA 1990].

PERSONAL HYGIENE

If benzidine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water. Get medical help immediately.

Clothing contaminated with benzidine should be removed immediately and should then be discarded.

A worker who handles benzidine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where benzidine or a solution containing benzidine is handled, processed, or stored.

STORAGE

Control, handling, processing, and storing of benzidine must be performed in accordance with OSHA's standard for benzidine [29 CFR 1910.1010]. This substance should be isolated in closed systems and should be well ventilated at the points where the system is opened. Containers should be kept closed and be protected from light.

SPILLS

Treat any benzidine spill as an emergency. Preplan for benzidine spills and have a trained team ready to respond in an emergency. Cleanup personnel should be clothed and

equipped in a manner that prevents any contact with benzidine.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Benzidine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for benzidine is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of benzidine per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of benzidine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Benzidine is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U021. This substance has been banned from land disposal and may be treated by incineration. Benzidine also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of benzidine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or

repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with benzidine. All skin and mucous membrane contact with benzidine should be prevented by the wearing of full-body protective clothing and gloves. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with benzidine. Contact lenses should not be worn if the potential exists for benzidine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZOYL PEROXIDE

INTRODUCTION

This guideline summarizes pertinent information about benzoyl peroxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{14}H_{10}O_4$

- **Structure**

$(C_6H_5CO)_2O_2$

- **Synonyms**

Benzoic acid, benzoperoxide; benzoyl superoxide; diphenylglyoxal peroxide; dibenzoyl peroxide; Acetoxyl; Acnegel; Benzac; Clearasil BP Acne Treatment; Cuticura Acne Cream; Debroxide; Dry and Clear Acne Cream; Epiclear; Fostex; Incidol; Lucidol; Luperco AA; Nayper B; Novadelox; Oxy-5; Oxy Wash; Panoxyl; Persadox; Quinolor Compound; Sulfoxyl; Topex; Vanoxide; Xerac

- **Identifiers**

1. CAS No.: 94-36-0
2. RTECS No.: DM8575000 (for the technical product)
3. DOT UN: 2085 49 (for the technical product)
4. DOT label: Organic Peroxide

- **Appearance and odor**

Benzoyl peroxide is a white crystalline solid that has a faint benzaldehyde odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 242.2
2. Boiling point (at 760 mm Hg): Decomposes explosively at temperatures above 105°C (221°F)
3. Specific gravity (water = 1): 1.33 at 25°C (77°F)
4. *Vapor density:* Not applicable
5. Melting point: 103° to 105°C (217.4° to 221°F)
6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg
7. *Solubility:* Sparingly soluble in water, alcohol, or vegetable oils; soluble in chloroform, ether, and benzene
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, friction, or impact. Confined storage of dry benzoyl peroxide may lead to decomposition and explosion.
2. *Incompatibilities:* Benzoyl peroxide is extremely reactive, and fires and explosions may result from contact with strong acids, oxidizing and reducing agents, metals, metal oxides, amines, accelerators, methyl methacrylate, organic matter, carbon tetrachloride and ethylene, dimethylaniline, or lithium aluminum hydride.
3. Hazardous decomposition products: Toxic gases, vapors, and particulates (such as benzoic acid, phenyl benzoate, terphenyls, biphenyls, benzene, carbon monoxide, and carbon dioxide) may be released when benzoyl peroxide decomposes.
4. *Special precautions:* Benzoyl peroxide is highly reactive and may explode spontaneously; it must be kept wet in a mixture containing at least 1% water.

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• **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to benzoyl peroxide.

1. Flash point: 80°C (176°F)

2. Autoignition temperature: 80°C (176°F)

3. Flammable limits in air: Data not available

4. Extinguishant: Use water only; do ***not*** use chemical or carbon dioxide extinguishants.

Fires involving benzoyl peroxide should be fought from an explosionproof location. In advanced or massive fires, the area should be evacuated. Isolate the hazard area and deny access to unnecessary personnel. If fire occurs in the vicinity of containers of benzoyl peroxide, water should be used to keep containers cool. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving benzoyl peroxide.

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzoyl peroxide is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workshift and a 40-hr workweek [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned benzoyl peroxide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• **Rationale for limits**

The limits are based on the risk of respiratory irritation associated with exposure to benzoyl peroxide.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to benzoyl peroxide can occur through inhalation, ingestion, or contact with the skin or eyes.

• **Summary of toxicology**

1. *Effects on Animals*: Benzoyl peroxide is an irritant of the eyes, mucous membranes, and skin in animals. When instilled into the eyes of rabbits, benzoyl peroxide dust caused irritation [IARC 1985]. A 10% solution of benzoyl peroxide applied to the skin of guinea pigs caused a moderate degree of skin irritation [IARC 1985]. In rats, the 4-hr LC_{50} is estimated to be 700 ppm, and the oral LD_{50} is 7,710 mg/kg [ACGIH 1991a; NIOSH 1991]. During an acute 4-hr exposure to 2,458 ppm (24,300 mg/m^3), rats showed eye tearing and squinting, difficult breathing, excessive salivation, erythema, and motor excitation followed by depression; all animals recovered within the 24- or 48-hr period following termination of exposure [NIOSH 1977]. In a chick embryo assay, embryo toxicity and malformations were induced by benzoyl peroxide [NLM 1991]. Chronic feeding studies in rats showed decreased weight gain in the medium- and high-dose groups and testicular atrophy among males in the high-dose group [IARC 1985].

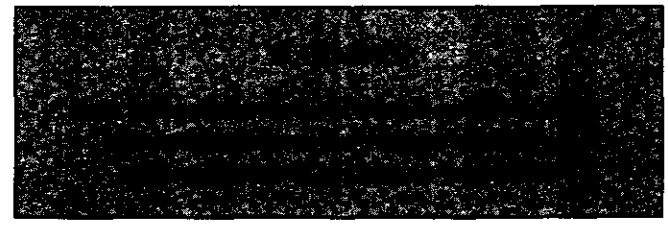
2. *Effects on Humans*: Benzoyl peroxide is an irritant of the eyes, skin, and mucous membranes in humans. This substance is also a skin sensitizer. Workers exposed to 12.2 mg/m^3 experienced strong irritation of the nose and upper respiratory tract [Proctor et al. 1988]. In prolonged and repeated contact with the skin, benzoyl peroxide has caused dermal irritation and sensitization [IARC 1985].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to benzoyl peroxide can cause moderate to severe irritation of the eyes, nose, and throat, with redness and tearing of the eyes, runny nose, cough, and difficult breathing. In contact with the skin, benzoyl peroxide causes redness and swelling.

2. *Chronic exposure*: Chronic exposure to benzoyl peroxide can cause dermatitis. Some sensitized individuals may also experience whorls, swelling, itching, and redness of the skin.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if benzoyl peroxide is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of benzoyl peroxide may result in worker exposures to this substance:

—Use as an initiator in free radical polymerization

—Use in production of polystyrene and related resins

—Use in auto-repair kits, optical and dental castings, and other molding applications

—Use in vulcanization of natural and synthetic rubbers

—Use in textile manufacture as a burn-out agent for cellulose acetate to produce lace-like appearance in mixed fabrics

—Use in printing pastes

—Use in topical non-prescription medications as a treatment of acne, burns, dermatitis, poisoning, and external wounds, and as an antiseptic and local anesthetic

—Use as a bleaching agent for flour, cheese, fats, oils, and waxes

—Use in the manufacture of special fast-drying inks for printing on plastic surfaces and in the embossing of vinyl flooring

—Use as a fixing agent in light microscopy

The following methods are effective in controlling worker exposures to benzoyl peroxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to benzoyl peroxide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and

physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract and skin and on a history of skin allergies. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to benzoyl peroxide at or below the prescribed exposure limit. The examining licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health licensed medical practitioner. Additional examinations may be necessary if a worker develops symptoms attributable to benzoyl peroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of benzoyl peroxide on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for benzoyl peroxide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne benzoyl peroxide is determined by using a cellulose ester membrane filter (0.8 micron). Samples are collected at a maximum flow rate of 3 liters/min until a maximum air volume of 400 liters is collected. Immediately after sampling, the sample filters are transferred into a 20-ml scintillation vial and are then sealed and shipped under refrigeration. Upon receipt by the laboratory, the samples are frozen until they are to be analyzed. The sample is then treated with ethyl ether to extract the benzoyl peroxide. Analysis is conducted by high-performance liquid chromatography using ultraviolet light detection. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method 5009 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If benzoyl peroxide contacts the skin, workers should remove any contaminated clothing immediately while drenching the affected area with water and then wash with soap and water.

Clothing and shoes contaminated with benzoyl peroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of benzoyl peroxide.

A worker who handles benzoyl peroxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where benzoyl peroxide is handled, processed, or stored.

STORAGE

Benzoyl peroxide should be stored in a cool, dry, well-ventilated, fireproof area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Isolated, remote, or detached storage is preferred. The storage area should be equipped with an automatic fire suppression system. To prevent static sparks, all containers and equipment used in shipping, receiving, or transferring operations should be bonded and grounded. Only nonsparking tools may be used with benzoyl peroxide. Any storage system should have an explosion-relief design, and electrical installations and heating facilities should be prohibited in these storage areas. Only the small amount of benzoyl peroxide that is needed for a single work shift should be removed from storage at one time. Containers of benzoyl peroxide should be protected from incompatible chemicals, physical damage, shock, rough handling, friction,

sunlight, heat, sparks, and open flame. Because containers that formerly contained benzoyl peroxide may still hold product residues, they should be handled appropriately.

SPILLS

Before benzoyl peroxide is used in the workplace, an emergency plan to handle any contingencies, including spills, should be developed and practiced. In the event of a spill involving benzoyl peroxide, the plan should be implemented. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres using maximum explosionproof ventilation.
5. Cleanup personnel must wear fire-resistant and antistatic protective clothing.
6. Use nonsparking tools for cleanup. Do ***not*** use cellulosic materials (rags, paper, straw, etc.) to clean up spilled benzoyl peroxide.
7. All benzoyl peroxide spills should be inactivated by adding cold, 10% sodium hydroxide solution to the spilled material in an amount equal to 10 times the weight of the spill. This process takes up to 3 hr to complete.

SPECIAL REQUIREMENTS

The U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Benzoyl peroxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of benzoyl peroxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of benzoyl peroxide per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of benzoyl peroxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although benzoyl peroxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of benzoyl peroxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular

respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Fire- and static-resistant protective clothing should be worn to prevent skin contact with benzoyl peroxide. Gloves, boots, aprons, and gauntlets are recommended to prevent prolonged or repeated skin contact. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to benzoyl peroxide permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to benzoyl peroxide.

If benzoyl peroxide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which benzoyl peroxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with benzoyl peroxide. Contact lenses should not be worn if the potential exists for benzoyl peroxide exposure.

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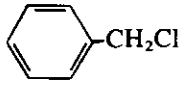
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about benzyl chloride for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_7H_7Cl
- **Structure:** 
- **Synonyms:** Alpha-chlorotoluene, chloromethylbenzene
- **Identifiers:** CAS 100-44-7; RTECS XS8925000; DOT 1738, label required: "Poison, Corrosive"
- **Appearance and odor:** Colorless to slightly yellow liquid with a pungent, aromatic, irritating odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 126.58
2. Boiling point (at 760 mmHg): 179.4°C (355°F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of benzyl chloride): 4.36
5. Melting point: -39.2°C (-38.6°F)
6. Vapor pressure at 22°C (71.6°F): 1 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.05
8. Evaporation rate (butyl acetate = 1): 0.11
9. Saturation concentration in air (approximate) at 22°C (71.6°F): 0.13% (1300 ppm)

- **Reactivity**

1. Incompatibilities: Contact with active metals such as copper, aluminum, magnesium, iron, zinc, and tin may cause the liberation of heat and hydrogen chloride. Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving benzyl chloride.
3. Caution: Benzyl chloride will attack some forms of plastic, rubber, and coatings.

- **Flammability**

1. Flash point: 67°C (153°F) (closed cup)
2. Autoignition temperature: 585°C (1085°F)
3. Flammable limits in air, % by volume: Lower, 1.1; Upper, Not available
4. Extinguishant: Dry chemical, foam, carbon dioxide, or water spray
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.04 ppm
2. Eye irritation level: 16 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor and irritant effects, benzyl chloride can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzyl chloride is 1 part of benzyl chloride per million parts of air (ppm) [5 milligrams of benzyl chloride per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 1 ppm (5 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 1 ppm (5 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for benzyl chloride

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	1	5
NIOSH REL Ceiling (15 min)	1	5
ACGIH TLV® TWA	1	5

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Benzyl chloride may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• **Summary of toxicology**

1. *Effects on animals:* Acute subcutaneous injection of benzyl chloride in rats caused labored breathing, bloody diarrhea, lung edema with bleeding, and liver damage. Acute inhalation of benzyl chloride by cats caused irregular respiration, inactivity, marked unresponsiveness, and death due to hemorrhage in the lungs; the surviving cats later developed clouded corneas, conjunctivitis, and severe pneumonia. Chronic subcutaneous injection of benzyl chloride in rats produced injection-site skin cancer and lung metastases. Oral administration of benzyl chloride to rats during pregnancy caused increased embryolethality and retarded postnatal development. NIOSH will continue to monitor the research regarding benzyl chloride to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.

2. *Effects on humans:* Long-term exposure of workers to benzyl chloride has caused increased incidences of respiratory illness and dermatitis, abnormal liver function and serum protein levels, and decreased white blood cell counts. An increased incidence of lung cancer has been reported for workers potentially exposed to benzyl and benzoyl chlorides.

• **Signs and symptoms of exposure**

Short-term (acute): Exposure to benzyl chloride can cause weakness, persistent headache, irritability, sweating, tremors, and loss of sleep and appetite. Skin sensitization, intense inflammation of the mucous membranes, and corneal damage can also occur.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of revelant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to benzyl chloride, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, eyes, liver, and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to benzyl chloride at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to benzyl chloride. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, eyes, liver, and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according ot standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, tests of lung function, and chest X-rays.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to benzyl chloride may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of benzyl chloride. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual.*

• **Method**

Sampling and analysis may be performed by collecting benzyl chloride vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure benzyl chloride may also be used if available. A detailed sampling and analytical method for benzyl chloride may be found in the *NIOSH Manual of Analytical Methods* (method number 1003).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with benzyl chloride.

Workers should be provided with and required to use splash-proof safety goggles where benzyl chloride may come in contact with the eyes.

SANITATION

Clothing which is contaminated with benzyl chloride should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of benzyl chloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of benzyl cloride's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with benzyl chloride should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle benzyl chloride should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to benzyl chloride may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for benzyl chloride

Operations	Controls
During use in the production of benzyl compounds	Process enclosure, local exhaust ventilation, personal protective equipment
During use in polymerization as a reactant catalyst, accelerator, and promoter; during use in rubber adhesives and TV tubes	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a raw material for pickling inhibitors, gasoline gum inhibitors, and synthetic tanning agents; during use in the processing of starch and the preparation of textile fibers	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assitance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to benzyl chloride, an eye-wash fountain should be provided within the immediate work area for emergency use. If benzyl chloride gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to benzyl chloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If benzyl chloride gets on the skin, wash it immediately with soap and water. If benzyl chloride penetrates the clothing, re-

move the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If benzyl chloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing benzyl chloride, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from benzyl chloride vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing benzyl chloride may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Benzyl chloride should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing benzyl chloride may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for benzyl chloride

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 10 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)
	Any powered air-purifying respirator with organic vapor and acid gas cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any chemical cartridge respirator with organic vapor and acid gas cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor and acid gas canister
	Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
Planned or emergency entry into environments containing unknown concentrations or levels above 10 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor and acid gas canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 1 ppm (5 mg/m^3) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BERYLLIUM AND ITS COMPOUNDS POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about beryllium and its compounds for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** Be
- **Synonyms:** Synonyms vary depending upon specific compound
- **Identifiers:** CAS 7440-41-7; RTECS DS1750000; DOT 1567, label required: "Poison, Flammable Solid"
- **Appearance:** Silvery gray metal

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 9.01
2. Boiling point (at 760 mmHg): 2,970°C (5,378°F)
3. Specific gravity (water = 1): 1.85
4. Melting point: 1,283°C (2,341°F)
5. Insoluble in water

- **Reactivity**

1.Incompatibilities: Acids, alkalies, chlorinated hydrocarbons, and oxidizable agents

2. Hazardous decomposition products: Beryllium reacts with strong acids to evolve hydrogen.

- **Flammability**

1. Extinguishant: Sand, soda ash, or commercial metal fire extinguishant powder may be used. Do not use water or carbon dioxide.
2. Flammability Rating 1 (NFPA)
3. Caution: Powdered beryllium is flammable in air. Hazard increases as fineness of powder increases.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for beryllium and its compounds is 2 micrograms of beryllium per cubic meter of air ($\mu g/m^3$) as a time-weighted average (TWA) concentration over an 8-hour workshift; the acceptable ceiling concentration is 5 $\mu g/m^3$; and the maximum peak concentration above the acceptable ceiling concentration (maximum duration of 30 minutes) is 25 $\mu g/m^3$. The National Institute for Occupational Safety and Health (NIOSH) recommends that beryllium be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible level. The NIOSH recommended exposure limit (REL) is that occupational exposure to beryllium be controlled so that no worker will be exposed in excess of 0.5 $\mu g/m^3$. The NIOSH REL is the lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated beryllium as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 2 $\mu g/m^3$ as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for beryllium

	Exposure limits $\mu g/m^3$
OSHA PEL TWA	2
Acceptable ceiling	5
Maximum peak above ceiling (30 min)	25
NIOSH REL (Ca)*	
No exposure in excess of	0.5
ACGIH TLV® TWA (A2)†	2

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Beryllium may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

• **Summary of toxicology**

1. *Effects on animals:* Chronic inhalation or intratracheal injection of beryllium metal or its compounds produced lung cancer in rats. Single intrabronchial implantations of beryllium oxide or chronic inhalation of beryllium sulfate produced lung cancer in monkeys. In rabbits, intraosseous administration of beryllium metal or its compounds produced bone cancer.

2. *Effects on humans:* Acute or chronic inhalation of beryllium has caused rhinitis (inflammation of the mucous membranes of the nose), tracheobronchitis (inflammation of the trachea and bronchi), pneumonitis (inflammation of the lungs), and death due to pulmonary edema or heart failure. Chronic inhalation of beryllium has been associated with kidney stones; enlargement of the liver, spleen, and heart; multiple granulomas of the lung, spleen, liver, and lymph nodes; and an increased incidence of lung cancer.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to beryllium can cause pain below the sternum, weight loss, nonproductive cough, shortness of breath, and irritation of the eyes, respiratory system, and skin.

2. *Long-term (chronic):* Exposure to beryllium can cause cough, pain in the joints, general weakness, weight loss, clubbing of fingers, shortness of breath, cyanosis, and allergic contact dermatitis. Accidental implantation of beryllium metal or crystals into the skin can cause tissue necrosis and ulceration.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to beryllium, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, spleen, and cardiovascular and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to beryllium at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and significant breathing impairment due to preexisting chronic lung disease. Skin patch testing with soluble beryllium compounds is *not* recommended because of the risk of sensitization.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to beryllium. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, liver, kidneys, spleen, and cardiovascular and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires, tests of lung function, and chest X-rays. In the event of the occurrence of a chronic respiratory disease, diagnostic tests such as the lymphocyte transformation test may be useful in determining the role of beryllium sensitization.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to beryllium may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include: Contact and/or allergic dermatitis.

2. Delayed-onset SHE's include: Chronic beryllium disease of the lungs.

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting beryllium with cellulose membrane filters followed by digestion with acid and analysis by flameless atomic absorption with a graphite furnace. A detailed sampling and analytical method for beryllium may be found in the *NIOSH Manual of Analytical Methods* (method number 7102).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with beryllium.

SANITATION

Clothing which is contaminated with beryllium should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of beryllium from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of beryllium's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with beryllium should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle beryllium should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to beryllium may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for beryllium

Operations	Controls
During use in the manufacture of electrical components and ceramics	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the production of beryllium metal from ore	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the production of alloy	Process enclosure, local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to beryllium, an eye-wash fountain should be provided within the immediate work area for emergency use.

If beryllium gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

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Where there is any possibility of a worker's body being exposed to beryllium, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If beryllium gets on the skin, wash it immediately with soap and water. If beryllium penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

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Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If beryllium is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.

3. For small quantities of liquids containing beryllium or beryllium compounds, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing beryllium or beryllium compounds may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Beryllium dust may be collected by vacuuming with an appropriate high-efficiency filtration system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

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U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

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Table 3.—Respiratory protection for beryllium

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BISMUTH TELLURIDE DOPED WITH SELENIUM SULFIDE

INTRODUCTION

This guideline summarizes pertinent information about doped bismuth telluride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

Bi_2Te_3 doped with Bi_2Se_3, SnTe, and Te

- **Synonyms**

Doped bismuth sesquitelluride, doped bismuth tritelluride, doped dibismuth tritelluride, doped tellurobismuthite

- **Identifiers**

1. CAS No.: 1304-82-1
2. RTECS No.: EB3110000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Bismuth telluride doped with selenium is a nonflammable, gray, crystalline solid that has been enhanced (or doped) with a small amount of a selenium compound; doping confers on the semiconductor the charge characteristics of the doping agent, which alters the conductivity of the semiconductor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 800.76
2. Boiling point: Data not available
3. Specific gravity (water = 1): 7.7 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 573°C (1,063.4°F)
6. Vapor pressure: Not applicable
7. Solubility: Insoluble in water; decomposes in nitric acid
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: A violent reaction may result from contact of doped bismuth telluride with strong oxidizers (such as bromine, fluorine, or chlorine), and a toxic gas may evolve from contact with moisture.
3. Hazardous decomposition products: Toxic materials (such as tellurium) may be released in a fire involving doped bismuth telluride.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to doped bismuth telluride; this substance is not flammable.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant suitable for the materials involved in the surrounding fire.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving doped bismuth telluride.

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bismuth telluride doped with selenium sulfide is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established an 8-hr TWA of 5 mg/m^3 as the recommended exposure limit (REL) for bismuth telluride doped with selenium sulfide [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bismuth telluride doped with selenium sulfide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• **Rationale for limits**

The limits are based on the risk of respiratory effects associated with exposure to doped bismuth telluride.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to doped bismuth telluride can occur through inhalation, eye or skin contact, and ingestion.

• **Summary of toxicology**

1. *Effects on Animals*: Selenium-doped bismuth telluride causes reversible, nonfibrotic lesions in the lungs of exposed experimental animals [Clayton and Clayton 1981]. Dogs, rabbits, and rats were exposed to 15 mg/m^3 of a dust (average particle size 1.04 microns) containing a mixture of doped bismuth telluride and stannous telluride for 6 hr/day, 5 days/week for 1 year. The dogs and rabbits developed small granulomatous lesions in the lungs, and the rats developed epithelialization of the alveolar walls [ACGIH 1991a; Clayton and Clayton 1981]. Fibrotic changes did not occur in any species; in dogs examined 4 months after the cessation of exposure, these lesions had regressed, indicating reversibility [ACGIH 1991a; Clayton and Clayton 1981].

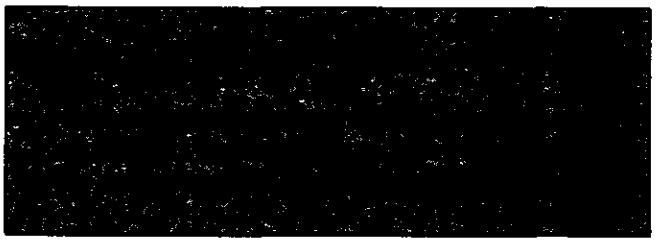
2. *Effects on Humans*: No adverse effects of exposure to doped bismuth telluride have been noted in humans except for the development of "tellurium breath" (breath that smells like garlic) [Clayton and Clayton 1981]. Based on effects seen in animals, overexposure to the dust of doped bismuth telluride is likely to cause reversible pulmonary changes in humans [Proctor et al. 1988].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to doped bismuth telluride can cause garlic breath and local irritation of the eyes and skin.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to doped bismuth telluride have been reported in humans.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: If a large amount of doped bismuth telluride is ingested take the following steps:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

Use of doped bismuth telluride as a semiconductor may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to doped bismuth telluride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to doped bismuth telluride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to doped bismuth telluride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

• Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employ-

ment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to doped bismuth telluride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of doped bismuth telluride on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for doped bismuth telluride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and the selected physiologic or laboratory tests conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne selenium-doped bismuth telluride (measured as bismuth) is determined by using a mixed cellulose ester filter (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989] and in the OSHA Computerized Information System [OSHA 1990].

PERSONAL HYGIENE

If the dust of doped bismuth telluride collects on the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with doped bismuth telluride should be removed.

A worker who handles doped bismuth telluride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where doped bismuth telluride is handled, processed, or stored.

STORAGE

Doped bismuth telluride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of doped bismuth telluride should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained doped bismuth telluride may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving doped bismuth telluride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Doped bismuth telluride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of doped bismuth telluride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of doped bismuth telluride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although doped bismuth telluride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of doped bismuth telluride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with doped bismuth telluride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to doped bismuth telluride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to doped bismuth telluride.

If doped bismuth telluride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which doped bismuth telluride might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with doped bismuth telluride.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BISMUTH TELLURIDE, UNDOPED

INTRODUCTION

This guideline summarizes pertinent information about undoped bismuth telluride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

Bi_2Te_3

- **Synonyms**

Bismuth sesquitelluride, bismuth tritelluride, dibismuth tritelluride, tellurobismuthite

- **Identifiers**

1. CAS No.: 1304-82-1
2. RTECS No.: EB3110000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Undoped bismuth telluride is a gray, crystalline solid that is not flammable.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 800.76
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 7.7 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 573°C (1,063.4°F)
6. Vapor pressure at 20°C (68°F): Not applicable
7. Solubility: Insoluble in water; decomposes in nitric acid
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: A violent reaction may result from contact of undoped bismuth telluride with strong oxidizers (such as bromine, fluorine, or chlorine), and a toxic gas may evolve from contact with moisture.
3. Hazardous decomposition products: Toxic materials (such as tellurium) may be released in a fire involving undoped bismuth telluride.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to undoped bismuth telluride; this substance is not flammable.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving undoped bismuth telluride.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for undoped bismuth telluride is 15 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for undoped bismuth telluride of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as an 8-hr TWA [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned undoped bismuth telluride a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• **Rationale for limits**

The limits are based on the risk of physical irritation associated with exposure to undoped bismuth telluride.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to undoped bismuth telluride can occur through inhalation, eye or skin contact, and ingestion.

• **Summary of toxicology**

1. *Effects on Animals*: Dogs, rabbits, and rats exposed to undoped bismuth telluride dust (average particle size 0.4 micron) at 15 mg/m^3 for 6 hr/day, 5 days/week for 11 months showed no adverse responses other than accumulation of this substance in the lungs [Cralley and Cralley 1985].

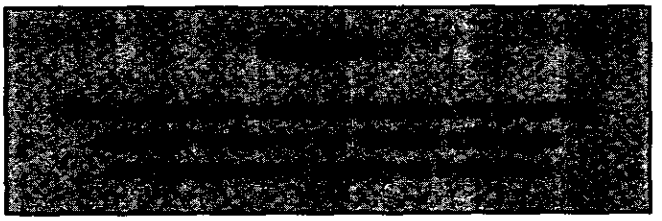
2. *Effects on Humans*: In humans, exposure to the dust of undoped bismuth telluride causes physical irritation of the eyes, nose, and throat [NJDH 1985]. Long-term exposure causes accumulation of dust in the lungs; this dust is radiographically visible [NJDH 1985].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to undoped bismuth telluride can cause local irritation of the eyes and skin.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to undoped bismuth telluride have been reported.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if undoped bismuth telluride is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of undoped bismuth telluride may result in worker exposures:

—Use for thermoelectric cooling

—Use as a semiconductor

The following methods are effective in controlling worker exposures to undoped bismuth telluride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to undoped bismuth telluride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to undoped bismuth telluride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to undoped bismuth telluride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of undoped bismuth telluride on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for undoped bismuth telluride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne undoped bismuth telluride (measured as bismuth) is determined by using a mixed cellulose ester filter (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989] and in the OSHA Computerized Information System [OSHA 1990].

PERSONAL HYGIENE

If the dust of undoped bismuth telluride collects on the skin in excessive amounts, workers should wash the affected areas with soap and water.

Clothing contaminated with the dust of undoped bismuth telluride should be removed.

A worker who handles undoped bismuth telluride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where undoped bismuth telluride is handled, processed, or stored.

STORAGE

Undoped bismuth telluride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [40 CFR 1910.1200]. Containers of undoped bismuth telluride should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained undoped bismuth telluride may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving undoped bismuth telluride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill.
5. Use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area for reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Undoped bismuth telluride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of undoped bismuth telluride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of undoped bismuth telluride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although undoped bismuth telluride is not specifically listed as

a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of undoped bismuth telluride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with undoped bismuth telluride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to undoped bismuth telluride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to undoped bismuth telluride.

If undoped bismuth telluride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which undoped bismuth telluride might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with undoped bismuth telluride.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BORON OXIDE

INTRODUCTION

This guideline summarizes pertinent information about boron oxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

B_2O_3

- **Synonyms**

Anhydrous boric acid, boric anhydride, boric oxide, boron sesquioxide, boron trioxide, diboron trioxide, fused boric acid

- **Identifiers**

1. CAS No.: 1303-86-2
2. RTECS No.: ED7900000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Boron oxide is a noncombustible, odorless, colorless or white, brittle substance that occurs as hygroscopic granules or in flake or powder form.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 69.6
2. Boiling point (at 760 mm Hg): 1,842°C (3,380°F)
3. Specific gravity: 2.5 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 450°C (842°F)
6. Vapor pressure at 20°C (68°F): Approximately 0 mm Hg
7. Solubility: Soluble in ethanol, glycerol, and hot water; slightly soluble in cold water
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Boron oxide reacts slowly with water to form boric acid.
2. Incompatibilities: Fires and explosions may result from contact of boron oxide with bromine pentafluoride or calcium oxide.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

This substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving boron oxide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving boron oxide.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for boron oxide is 10 mg/m^3 (total dust) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for boron oxide of 10 mg/m^3 as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned boron oxide a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye and upper respiratory tract irritation associated with exposure to boron oxide.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to boron oxide can occur through inhalation, ingestion, or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Boron oxide is an irritant of the skin and mucous membranes in animals. The oral LD_{50} in mice is 3,163 mg/kg [NIOSH 1991]. Application of boron oxide dust to the shaved skin of rabbits caused redness that persisted for several days [Wilding et al. 1959]. When instilled into the eyes of rabbits, the dust caused conjunctivitis [Wilding et al. 1959]. Rats exhibited mild nasal irritation when exposed to a boron oxide aerosol at 470 mg/m^3 for 6 hr/day, 5 days/week for 10 weeks [NLM 1991; ACGIH 1991a]. Young rats intubated with a 10% boron oxide slurry for 3 weeks showed no adverse effects [ACGIH 1991a].

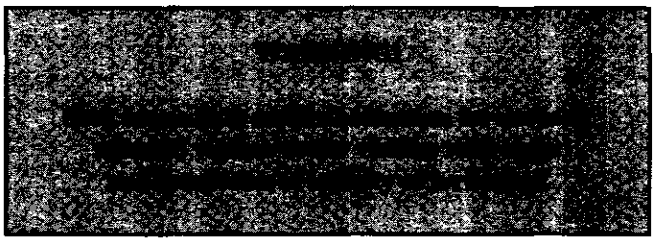
2. *Effects on Humans*: Exposure to boron oxide causes irritation of the eyes and respiratory tract; dryness of the mouth, nose, and throat; sore throat; and a productive cough [Garabrant et al. 1984]. A group of 113 workers exposed to the dust of boron oxide and boric acid at mean concentrations of 4.1 mg/m^3 (range 1.2 to 8.5 mg/m^3; exposures occasionally in excess of 10 mg/m^3) exhibited statistically significant increases in eye, nose, and upper respiratory tract symptoms [Garabrant et al. 1984].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to boron oxide can cause pain and redness of the eyes, tearing, irritation of the nasal membranes, sore throat, and cough.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to boron oxide have been reported.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if boron oxide is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve boron oxide and may result in worker exposures to this substance:

—Preparation of fluxes for enamels and glazes

—Laboratory analysis of silicates

—Manufacture of glass for heat-resistance

—Use of boron oxide in blowpipe analysis

—Application as a herbicide

—Production of surface coatings and use of boron oxide in the electronics industry

—Production of boron, boron master alloys, borides, metal borates, and boron carbide, nitrides, and halides

—Use of boron oxide as an additive to provide fire-resistance to enamels, paints, and insulation

—Use of boron oxide as an additive for glass fibers

The following methods are effective in controlling worker exposures to boron oxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to boron oxide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to boron oxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye or skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to boron oxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of boron oxide on the eyes or skin. Current health status should be compared with the

baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Serum borate concentrations are qualitative indicators of exposure to borate compounds (including boron oxide), but these levels cannot be correlated with airborne concentrations of borates. Therefore, no biological monitoring test acceptable for routine use has yet been developed for boron oxide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne boron oxide is determined by using tared, low-ash polyvinyl chloride filters (5-micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. This is a gravimetric field test method based on the total weight collected and does not need to be submitted to the laboratory for analysis. This method is described in the section on filter weighing procedures in the *OSHA Chemical Information Manual* [OSHA 1987]. Additional information can be found in Method 0500 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If boron oxide contacts the skin, workers should flush the affected areas immediately with plenty of water for at least 15 min and then wash with soap and water.

Clothing contaminated with boron oxide should be removed promptly.

A worker who handles boron oxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where boron oxide or a solution containing boron oxide is handled, processed, or stored.

STORAGE

Boron oxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of boron oxide should be protected from physical damage, kept dry, and stored separately from bromine pentafluoride or calcium oxide, heat, sparks, and open flame. Because containers that formerly contained boron oxide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving boron oxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill.

1. Scoop up spilled material and place the material in a covered container for later reclamation or disposal.

2. Avoid generating dust during cleanup by using a vacuum or a wet method.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Boron oxide is not subject to EPA emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of boron oxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form

(Form R) to EPA reporting the amount of boron oxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although boron oxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of boron oxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent repeated skin contact with boron oxide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to boron oxide permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to boron oxide.

If boron oxide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which boron oxide might contact the eyes (e.g., through dust particles or splashes of boric acid). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with boron oxide. Contact lenses should not be worn if the potential exists for boron oxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BORON TRIBROMIDE

INTRODUCTION

This guideline summarizes pertinent information about boron tribromide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

BBr_3

- **Synonyms**

Boron bromide; tribromoborane, trona

- **Identifiers**

1. CAS No.: 10294-33-4
2. RTECS No.: ED7400000
3. DOT UN: 2692 59
4. DOT label: Corrosive

- **Appearance and odor**

Boron tribromide is a colorless, fuming, nonflammable, volatile liquid with a sharp, irritating odor. No quantitative data are available on the odor threshold for boron tribromide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 250.6
2. Boiling point (760 mm Hg): 90°C (194°F)
3. Specific gravity (water = 1): 2.7 at 0°C (32°F)
4. Vapor density (air = 1 at boiling point of boron tribromide): 8.6
5. Melting point: -46°C (-51°F)
6. Vapor pressure at 33.5°C (92.3°F), 100 mm Hg; at 14°C (57.1°F), 40 mm Hg
7. Solubility: Decomposes in water or alcohol; soluble in carbon tetrachloride and sulfur dioxide
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat and moisture
2. Incompatibilities: Fire and explosions may result from contact of boron tribromide with water, steam, potassium, sodium, or alcohol.
3. Hazardous decomposition products: Toxic gases and particulates (such as hydrogen bromide, oxides of boron, and oxides of bromine) may be released in a fire involving boron tribromide.
4. Special precautions: Boron tribromide attacks metals, wood, rubber, and Bakelite® but does not attack Teflon® or stainless steel.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to boron tribromide; this substance is not combustible.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving boron tribromide should be fought upwind and from the maximum distance possible. Isolate the hazard

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area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Containers of boron tribromide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving boron tribromide. Firefighters' protective clothing may not provide protection against permeation by boron tribromide.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for boron tribromide is 1 ppm (10 mg/m^3) as a ceiling limit. A worker's exposure to boron tribromide shall at no time exceed this limit [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (10 mg/m^3) as a ceiling limit [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned boron tribromide a threshold limit value (TLV) of 1 ppm (10 mg/m^3) as a ceiling limit that should not be exceeded during any part of the working exposure [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of irritation associated with exposure to boron tribromide.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to boron tribromide can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: No acute toxicity data specific to boron tribromide is available. However, the toxicity and action of boron tribromide is similar to that of boron trichloride, which causes marked swelling and burns in contact with the eyes, skin, or mucous membranes; hemorrhages of the lungs, kidneys, and intestines in some animals acutely exposed to lethal concentrations; and death in all mice and rats exposed to 20 ppm for 7 hr [Clayton and Clayton 1981]. The LC_{50} for a 1-hr exposure to hydrogen bromide, a hydrolysis product of boron tribromide, is 814 ppm in the mouse and 2,858 ppm in the rat [Sax and Lewis 1989].

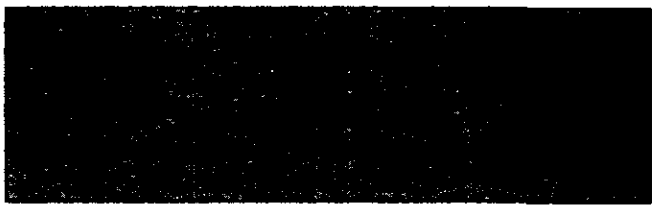
2. *Effects on Humans*: Boron tribromide is an irritant that is strongly corrosive because of its rapid hydrolysis to boric acid and hydrogen bromide [ACGIH 1991a; Clayton and Clayton 1981]. Acute exposure to boron tribromide causes marked irritation of the eyes, nose, throat, and skin, and contact of the eyes or skin with boron tribromide leads to burns [NJDH 1985]. Pulmonary edema, which is potentially life threatening, may result from acute respiratory exposure to boron tribromide [NJDH 1985]. A chemist who splashed boron tribromide into his eyes experienced no pain at the time but subsequently developed permanent corneal injury, including corneal opacification, in the most severely exposed eye; the other eye gradually returned to normal [Grant 1986].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to boron tribromide can cause redness, swelling, and tearing of the eyes; runny nose; coughing; and shortness of breath. Contact of this substance with the skin or eyes may lead to burns of the affected tissues.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to boron tribromide have been reported.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of boron tribromide! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of boron tribromide are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if boron tribromide or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve boron tribromide and may result in worker exposures to this substance:

—Use of boron tribromide as a catalyst in organic synthesis

—Production of diborane and ultra-high-purity boron

—Manufacture of semiconductors

The following methods are effective in controlling worker exposures to boron tribromide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to boron tribromide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be

aggravated or may result in increased risk when a worker is exposed to boron tribromide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to boron tribromide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of boron tribromide on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for boron tribromide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne boron tribromide is determined by using a midget fritted-glass bubbler containing 10 ml of 0.003M $NaHCO_3$/0.0024 M Na_2CO_3. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 5 liters is collected. Analysis is conducted by ion chromatography. The limit of detection for this procedure is 0.01 mg/m^3. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If boron tribromide contacts the skin, workers should immediately flood the affected areas with water and then wash with soap and water.

Clothing and shoes contaminated with boron tribromide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of boron tribromide, particularly its potential to cause skin burns.

A worker who handles boron tribromide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where boron tribromide or a solution containing boron tribromide is handled, processed, or stored.

STORAGE

Boron tribromide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of boron tribromide should be protected from physical damage and should be stored away from water, steam, potassium, sodium, alcohol, heat, sparks, and open flame. Because containers that formerly contained boron tribromide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving boron tribromide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use water spray to reduce vapors; do not put water directly on the leak or spill area.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the boron tribromide for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Boron tribromide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of boron tribromide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of boron tribromide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although boron tribromide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limits. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of boron tribromide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with boron tribromide. Full-body protection and gloves are recommended to prevent skin contact with this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Chlorinated polyethylene has demonstrated fair to good protection against permeation by boron tribromide.

If boron tribromide is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which boron tribromide might contact the eyes (e.g., through splashes of solution). Eyewash

fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with boron tribromide. Contact lenses should not be worn if the potential exists for boron tribromide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BORON TRIFLUORIDE

INTRODUCTION

This guideline summarizes pertinent information about boron trifluoride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

BF_3

- **Synonyms**

Trifluoroboron, boron fluoride, trifluoroborane

- **Identifiers**

1. CAS No.: 7637-07-2
2. RTECS No.: ED2275000
3. DOT UN: 1008 15
4. DOT label: Nonflammable Gas and Poison

- **Appearance and odor**

Boron trifluoride is a nonflammable, colorless gas that fumes in moist air and has a pungent, irritating odor. The odor threshold is reported to range from 1 to 1.5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 67.8
2. Boiling point (at 760 mm Hg): -100°C (-148°F)
3. Specific gravity (water = 1): 2.99 at 20°C (68°F)
4. Relative density (air = 1 at boiling point of boron trifluoride): 2.3
5. Melting point: -127.1°C (-196.8°F)
6. Vapor pressure at 20°C (68°F): Greater than 1 mm Hg
7. Solubility: Soluble in water and in most saturated and halogenated hydrocarbons and aromatic compounds; very soluble in concentrated acids and organic solvents
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Boron trifluoride hydrolyzes in moist air to boric acid, hydrogen fluoride, and fluoboric acid. It also decomposes in hot water to form boric acid and fluoboric acid. This substance also decomposes when heated.
2. Incompatibilities: Fires and explosions may result from contact of boron trifluoride with alkali metals, alkaline earth metals (except magnesium), alkyl nitrate, or calcium oxide. Boron trifluoride incandesces when heated with alkali metals or alkaline earth metals (except magnesium).
3. Hazardous decomposition products: Toxic gases and vapors (such as fluorine and fluorine compounds) may be released when boron trifluoride is heated to decomposition.
4. Special precautions: Boron trifluoride corrodes most metals in the presence of moisture.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to boron trifluoride; this substance is not flammable and will not support combustion.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Fires involving boron trifluoride should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of boron trifluoride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Do not get water inside containers. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Firefighters should wear a full set of protective clothing, including a self-contained breathing apparatus, when fighting fires involving boron trifluoride.

EXPOSURE LIMITS

• OSHA PEL

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for boron trifluoride is 1 ppm (3 mg/m^3) of air as a ceiling limit. A worker's exposure to boron trifluoride shall at no time exceed this ceiling limit [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (3 mg/m^3) as a ceiling limit [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned boron trifluoride a ceiling limit of 1 ppm (2.8 mg/m^3), which should not be exceeded during any part of the working day [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of severe pulmonary irritation associated with exposure to boron trifluoride.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to boron trifluoride can occur through inhalation and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Boron trifluoride is potentially a corrosive poisonous gas that can cause burns to the nasal and respiratory passages, eyes, and skin. It can also be dermally absorbed. Acute exposure of guinea pigs to 100 ppm resulted in the death of all animals. The 1-hr and 4-hr LC_{50}s for rats are 387 (320-467) and 393 ppm, respectively. Before the deaths of these animals, they exhibited respiratory irritation, pneumonia, kidney damage, retarded growth, and severe progressive dental fluorosis [NLM 1991]. In six studies, subchronic exposure of multiple species spanned 0.67 to 100 ppm for 0.5 to 6 months [NLM 1991]. Irritation was noted at all reported levels. Serum chemistry changes (dysproteinemia, decreased globulinemia and cholinesterase), nervous lability, decreased body weight, and pneumonitis occurred at 1 to 4 ppm over a 3 to 6 month exposure period. Rales, renal tubular necrosis, and death occurred at 6 ppm following 3 to 6 months of exposure. Progressive pulmonary involvement (difficult breathing, pneumonitis, emphysema, and alveolar collapse) and death from respiratory failure were noted during months 3 to 6 at 12.8 ppm. Increased lung and liver weights were noted in animals exposed to 22 or 60 ppm for 2 weeks. A 1-month exposure of six species to 100 ppm caused lung and kidney damage and the death of all animals [NLM 1991].

2. *Effects on Humans*: Boron trifluoride is a severe irritant of the nasal passages, lungs, skin, and eyes in humans, producing burns similar to those caused by hydrofluoric acid. Because this substance forms acids when it comes into contact with moisture, the eyes and skin can be severely burned if exposed to boron trifluoride. Exposure at 50 ppm for 30 to 60 min is believed to be lethal to humans [Braker and Mossman 1980]. Eight of 13 workers exposed for 1 to 27 years to boron trifluoride concentrations ranging from an estimated 0.1 to 1.8 ppm showed decreased pulmonary function (forced ventilatory capacity and expiratory volume) on clinical examination, although their chest X-rays were normal [Clayton and Clayton 1981]. A group of 78 workers exposed for 10 to 15 years to boron trifluoride at unspecified concentrations (estimated occasionally to be as high as 32 ppm) developed nosebleeds and dryness of the nasal mucosa, bleeding gums, dry and scaly skin, and joint pain. Concurrent exposures to ethylene and isobutylene were also reported [Parmeggiani 1983; Proctor et al. 1988].

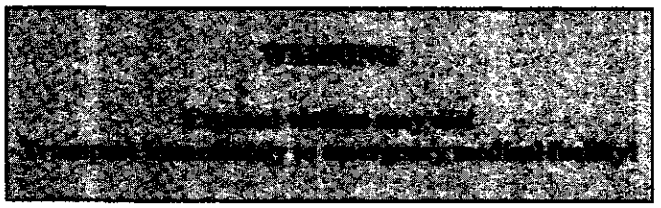
• Signs and symptoms of exposure

1. *Acute exposure*: Severe ambient exposure to boron trifloride can cause severe irritation or burns of the eyes, eyelids, and skin, inflammation and congestion of the lungs, cardiovascular collapse, respiratory failure, and death. Direct tissue contact with the gas can cause frostbite. Inhalation can induce severe salivation, nausea, gastritis, gastroenteritis, abdominal pain, retching, and prolonged vomiting with hematemesis, watery or tarry diarrhea, dehydration, shock, palor, cyanosis, coldness, rapid weak

pulse, rapid shallow breathing, drowsiness, hyporeflexia or convulsions, dilated pupils, coma, and death. Survivors may develop pyloric stenosis, hepatic cirrhosis, and renal damage.

2. *Chronic exposure*: Chronic exposure to boron trifluoride can cause nosebleeds and dryness of the nasal mucosa, bleeding gums, dry and scaly skin, joint pain, osteosclerosis, increased bone density and brittleness, mottled tooth enamel, weight loss, anemia, weakness, and decreased pulmonary function.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: If tissue is frozen, seek medical attention ***immediately***. In addition, tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: If frostbite occurs, seek medical attention ***immediately***. In addition, severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If boron trifluoride is inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of boron trifluoride may result in worker exposures to this substance:

—Use as a Lewis acid catalyst for alkylation of aromatic compounds and in the polymerization of phenolic and epoxy resins

—Use in nuclear technology for separation of boron isotopes, as a filling gas for neutron counters, in the production of neutron-absorbing salts for molten-salt breeder reactors, and in ionization chambers to detect weak neutrons

—Use as a fumigant

—Use in gas brazing and in the production of diborane and other boron-containing compounds

—Use in the electronics industry to treat separators for high-temperature cells, to prepare high-breakdown voltage varistors, and to enhance the surface conductivity of perylene

—Use in the magnesium industry during casting and heat-treating operations as a fire retardant and antioxidant

The following methods are effective in controlling worker exposures to boron trifluoride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to boron trifluoride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, kidneys, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to boron trifluoride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system, kidney, or skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to boron trifluoride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of boron trifluoride on the respiratory system, kidneys, and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urinary fluoride is a nonspecific indicator of exposure to a fluoride compound. Maintaining preshift and postshift urinary fluoride concentrations below 4 and 7 mg/g creatinine, respectively, appears to protect against the development of bony fluorosis.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to boron trifluoride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

Neither NIOSH nor OSHA has a recommended method for sampling boron trifluoride in the workplace. However, the following secondary analytical method, which has not been validated, is available. A worker's exposure to airborne boron trifluoride is determined by using a midget fritted-glass bubbler containing 10 ml of 0.1M ammonium fluoride. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 480 liters is collected. A stock standard is made by dissolving 0.125 g of potassium tetrafluoroborate in 100 ml of 0.1M ammonium fluoride. Working standards are then made by making serial dilutions of the stock standard in 0.1M ammonium fluoride to the appropriate ranges. Analysis is done using the fluoborate specific-ion electrode and a double junction reference electrode. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If boron trifluoride contacts the skin, the victim should immediately and thoroughly wash the affected areas with soap and water. Medical attention should be obtained immediately.

Clothing contaminated with boron trifluoride should be removed immediately. In case of massive exposure, the contaminated clothing should be removed under a drenching safety shower and medical attention should be obtained immediately.

A worker who is exposed to boron trifluoride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where boron trifluoride is present.

STORAGE

Boron trifluoride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage in a noncombustible structure is preferred. Cylinders should be stored and handled in accordance with OSHA's compressed gases standard [29 CFR 1910.101]. Containers of boron trifluoride should be protected from physical damage and should be stored separately from alkali metals, alkaline earth metals (except magnesium), alkyl nitrates, calcium oxide, heat, sparks, and open flame. Because containers that formerly contained boron trifluoride may still hold product residues, they should be handled appropriately.

LEAKS

Before boron trifluoride is used in the workplace, emergency procedures should be established and made known to all affected personnel. In the event of a leak involving boron trifluoride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Evacuate the leak area for at least 50 ft in all directions.
2. Notify safety personnel.
3. Stop the leak or remove the leaking cylinder if this can be done safely.
4. Do not get water inside cylinders containing boron trifluoride.
5. Flush the leak area with enough water to flood it.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Employers owning or operating a facility with 500 lb or more of boron trifluoride onsite must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for boron trifluoride is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of boron trifluoride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although boron trifluoride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of boron trifluoride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with boron trifluoride. Gloves, aprons, coveralls, long sleeves, and other protective equipment are recommended as necessary for workers exposed to boron trifluoride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to boron trifluoride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to boron trifluoride.

If boron trifluoride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which boron trifluoride gas might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with boron trifluoride. Contact lenses should not be worn if the potential exists for boron trifluoride exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMACIL

INTRODUCTION

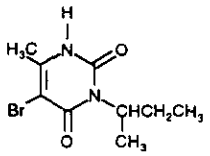
This guideline summarizes pertinent information about bromacil for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{13}BrN_2O_2$

- **Structure**



- **Synonyms**

Borea; bromazil; 5-bromo-6-methyl-3-(1-methyl propyl)-2,4(1*H*,3*H*)-pyrimidinedione; 5-bromo-6-methyl-3-(1-methylpropyl)-uracil; 5-bromo-3-sec-butyl-6-methyl-uracil; Cynogan; Eerex Granular Weed Killer; Eerex Water Soluble Concentrate Weed Killer; Herbicide 976; Hyvar; Hyvarex; isocil; Krovar II; Nalkil; Uragan; Uragon; Urox B.

- **Identifiers**

1. CAS No.: 314-40-9
2. RTECS No.: YQ9100000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Bromacil is an nonflammable, odorless, colorless-to-white, crystalline substance. It is commercially available as a wettable powder, liquid formulation, and mixture with various other agricultural chemicals. Bromacil-containing mixtures and liquid formulations may be combustible.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 261.11
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 1.55 at 25°C (77°F)
4. Vapor density: Data not available
5. Melting point: 157.5° to 160°C (313.7° to 320°F): slowly sublimes
6. Vapor pressure at 100°C (212°F): 0.0008 mm Hg
7. Solubility: Slightly soluble in water; moderately soluble in xylene, strong aqueous bases, acetone, acetonitrile, and ethanol; sparingly soluble in hydrocarbons.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame.
2. Incompatibilities: Decomposes slowly upon contact with strong acids.
3. Hazardous decomposition products: Toxic gases (such as bromine and oxides of nitrogen) may be released in a fire involving bromacil.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to bromacil. It may burn in its solid form,

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

but it does not ignite easily. Liquid formulations or mixtures containing bromacil may be combustible.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromacil.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromacil is 1 ppm (10 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 ppm (10 mg/m^3) as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromacil a threshold limit value (TLV) of 1 ppm (10 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of thyroid-damaging and irritant effects associated with exposure to bromacil.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to bromacil can occur through inhalation or ingestion.

• Summary of toxicology

1. *Effects on animals*: Bromacil is an irritant of the eyes and upper respiratory tract in experimental animals; this substance has also been shown to have endocrine and reproductive effects in rodents. When instilled into the eyes of rabbits, this substance caused reversible conjunctival irritation but no corneal damage [Grant 1986]. When applied to the skin of guinea pigs, bromacil caused mild to moderate irritation but was not a skin sensitizer [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is greater than 5 g/kg [NIOSH 1991]. The oral LD_{50} in rats is 641 mg/kg and does not induce signs or symptoms. Acute administration of 1,100 mg/kg to dogs induced salivation, vomiting, muscular weakness, excitability, diarrhea, and mydriasis. Chickens and cattle developed weight loss and abnormal gait following an oral dose of 250 mg/kg. Toxic symptoms in poisoned animals include anorexia, depression, tympanites, and increased respiratory rates. One dog survived a 5 g/kg dose [NLM 1992]. Male rats were given bromacil 5 days/week for 2 weeks at oral doses of 650, 1,035, or 1,500 mg/kg; 5 of 6 rats died after 5 doses at the highest level, 1 died after 10 doses at 1,035 mg/kg, and no animal died at the lowest dose. At autopsy, focal cell hypertrophy and hyperplasia of the liver were seen [NRC 1977]. Rats were fed bromacil at 50, 500, 2,500, 5,000, 6,000, or 7,000 ppm for 90 days; those in the 5,000-ppm or higher groups developed hyperthyroidism [NRC 1977]. In another study, rats were fed bromacil at 50, 250, or 1,250 ppm for 2 years; those in the 1,250-ppm group developed hyperplasia of the thyroid, and one female rat also developed a follicular adenoma [NRC 1977]. When pregnant rats were exposed by inhalation to 38 mg/m^3 (3.8 ppm) for 2 hr/day on gestation days 7 through 14, they developed reproductive, embryotoxic, and developmental effects [NIOSH 1991]. Conversely, rabbits that ingested diets containing 50 to 250 ppm bromacil during days 8 through 16 of pregnancy delivered normal pups. A three-generation rat study also demonstrated a lack of induced developmental toxicity [NLM 1992]. Contradictory mutagenicity results have been published for bromacil [NLM 1992]. A 2-yr chronic dietary study in rats did not result in cancer induction but did demonstrate that bromacil caused thyroid hyperplasia [NRC 1977]. All rats exposed to 4,800 mg/m^3 (480 ppm) bromacil for 4 hr survived [ACGIH 1991a].

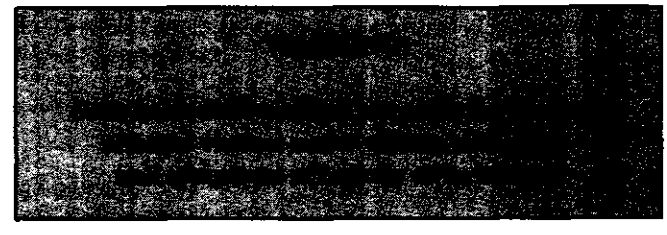
2. *Effects on humans*: Bromacil is known to cause eye, nose, and throat irritation in workers handling formulations containing this substance. Skin irritation has also been reported [NLM 1992; NJDH 1985]. There are no reports of bromacil-induced systemic toxicity.

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to bromacil dust can cause redness and itching of the eyes, runny nose, scratchy throat, and redness, dryness, and cracking of the skin.

2. *Chronic exposure*: No signs or symptoms of chronic bromacil exposure have been reported.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to particulates or to concentrated solutions, vapors, mists, or aerosols of bromacil. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If particulates or vapors, mists, or aerosols of bromacil are inhaled move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if bromacil or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations involve bromacil and may result in worker exposures to this substance:

—Manufacture or formulation of bromacil

—Use of bromacil as a herbicide to control annual and perennial grasses and broadleaf weeds

—Use of bromacil on noncrop lands as a nonselective herbicide and on a few crops (pineapple and citrus) as a selective herbicide

The following methods are effective in controlling worker exposures to bromacil, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to bromacil, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and

laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to bromacil at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or upper respiratory tract diseases.

- **Periodic medical examinations and biological monitoring.**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to bromacil exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromacil on the skin and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for bromacil.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne bromacil is determined by using a midget impinger containing 15 ml of ethylene glycol. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 50 liters is collected. Analysis is conducted by high-pressure liquid chromatography using an ultraviolet detector. This method is described in the *O*SHA Computerized Information System [OSHA 1990] and in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If bromacil contacts the skin, workers should wash the affected areas with soap and water.

Clothing and shoes contaminated with bromacil should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of bromacil, particularly its potential to cause irritation.

A worker who handles bromacil should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where bromacil is handled, processed, or stored.

STORAGE

Bromacil should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of bromacil should be protected from physical damage and should be stored separately from strong acids and heat. Because containers that formerly contained bromacil may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving bromacil, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.

5. For dry spills, use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area.

6. Absorb any spilled liquid containing bromacil with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Bromacil is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of bromacil; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromacil emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although bromacil is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromacil exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with bromacil. One source suggests wearing protective gloves and clothing when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to permeation by formulations containing bromacil. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protec-

tive clothing for workers to wear when they are exposed to bromacil.

If bromacil is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which bromacil might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with bromacil. Contact lenses should not be worn if the potential exists for bromacil exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMINE

INTRODUCTION

This guideline summarizes pertinent information about bromine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

Br_2

- **Synonyms**

Caswell No. 112

- **Identifiers**

1. CAS No.: 7726-95-6
2. RTECS No.: EF9100000
3. DOT UN: 1744 59
4. DOT label: Corrosive

- **Appearance and odor**

Bromine is a heavy, noncombustible, red-brown fuming liquid with an irritating and suffocating odor. The odor threshold is reported to be 0.05 to 3.5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Atomic number: 35
2. Molecular weight: 159.8
3. Boiling point (at 760 mm Hg): 58.8°C (137.8°F)
4. Specific gravity (water = 1): 3.1 at 20°C (68°F)
5. Vapor density (air = 1 at boiling point of bromine): 3.5
6. Melting point: −7.2°C (18.9°F)
7. Vapor pressure: 172 mm Hg at 20°C (68°F); 100 mm Hg at 9.3°C (48.7°F)
8. Solubility: Very slightly soluble in water; freely soluble in alcohol, ether, carbon tetrachloride, carbon disulfide, aqueous solutions of bromides, chloroform, and concentrated hydrochloric acid.
9. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Bromine emits toxic fumes when it is heated or in contact with steam or water.
2. Incompatibilities: Bromine is a powerful oxidizer; in contact with organic or other readily oxidizable materials, it may cause fires and explosions. Contact of liquid bromine with aqueous ammonia or with metals may cause violent reactions. Anhydrous bromine reacts violently with aluminum, titanium, mercury, or potassium. Bromine is also incompatible with alkali hydroxides, arsenites, carbonyls, alcohols, ferrous and mercurous salts, hypophosphites, and many other substances.
3. Hazardous decomposition products: Toxic fumes may be released in a fire involving bromine.
4. Special precautions: Bromine attacks some coatings and some forms of plastic and rubber. This substance corrodes iron, steel, stainless steel, and copper.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to bromine; however, it is a strong oxidizer and accelerates the burning of combustibles. The heat of such reactions may cause nearby combustible materials to ignite.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use dry chemical, carbon dioxide, Halon®, water spray, or alcohol foam to fight fires involving bromine. Because bromine can react with steam or with small amounts of water, containers should be cooled and surrounding fires should be extinguished by flooding with large amounts of water. Anhydrous ammonia vapor released from a safe distance can be used to neutralize large quantities of bromine vapor; do ***not*** use aqueous ammonia because it may react violently with liquid bromine.

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromine. Chemical protective clothing that is specifically recommended for bromine may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by bromine.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromine is 0.1 ppm (0.7 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 0.3 ppm (2 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.7 mg/m^3) as an 8-hr TWA and 0.3 ppm (2 mg/m^3) as a STEL [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromine a threshold limit value (TLV) of 0.1 ppm (0.7 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (2 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of severe irritation of the eyes, mucous membranes, lungs, and skin associated with exposure to bromine.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to bromine can occur through eye or skin contact, inhalation, and ingestion.

• Summary of toxicology

1. *Effects on Animals*: Bromine is a corrosive and severe irritant to the eyes, skin, mucous membranes, and respiratory tract in animals and can be rapidly fatal when inhaled. The lowest observed lethal concentration (LC_{Lo}) is 140 ppm for 7 hr in cats and guinea pigs and 180 ppm for 6.5 hr in rabbits [NIOSH 1991]. Cats, rabbits, and guinea pigs exposed to 180 ppm for 7 hr developed severe eye irritation with clouding of the cornea, severe irritation of the respiratory tract, and difficult breathing; at 23 ppm, however, the irritation and dyspnea was mild [NLM 1992]. Guinea pigs and rabbits exposed to 300 ppm for 3 hr developed lung edema, pseudomembranous deposits on the trachea and bronchi, and hemorrhages of stomach mucosa. Animals that died several days after this exposure showed evidence of bronchopneumonia and central nervous system disturbances at autopsy [Clayton and Clayton 1981]. The 2-hr and 9-min LC_{50}s for mice are 240 and 750 ppm, respectively [ACGIH 1991a; NLM 1992]. Rats, mice, and rabbits inhaling 0.2 ppm of bromine for 4 months showed disturbances in respiratory, endocrine, and nervous system functioning; exposure to 0.02 ppm for the same interval caused no adverse effects [NLM 1992]. Rats fed 0.01 mg/kg bromine for 6 months showed changes in conditional reflexes and in several blood indices.

2. *Effects on Humans*: Bromine is corrosive to the eyes, skin, mucous membranes, and respiratory tract in humans. Eye contact can result in severe, painful, and destructive burns of the eyes [Sittig 1985; AIHA 1978]. Brief contact of the skin with liquid bromine causes vesicles and pustules, and prolonged contact leads to deep, painful burns that ulcerate and are slow to heal [Sittig 1985; Clayton and Clayton 1981]. Repeated contact of the skin with bromine in liquid or vapor form may cause dermatitis and halogenacne [Rom 1983; Deichmann and Gerarde 1969]. Inhalation of airborne concentrations below 1 ppm causes tearing of the eyes; exposure to 4 ppm can be tolerated for only 30 to 60 min; 10 ppm induces respiratory damage and is considered immediately dangerous to life or health; and 30 ppm would cause death in a short time [Clayton and Clayton 1981; NIOSH 1987b; NLM 1992]. Acute nonlethal exposures can also induce coughing, nosebleed, feelings of oppression, dizziness, headache, and delayed onset of abdominal pain and measles-like dermal eruptions [NLM 1992]. Pulmonary edema may occur after several hours, and high concentrations can cause death from corrosive burns of the lung [Parmeggiani 1983; Sittig 1985]. The inhalation LC_{Lo} in humans is 1,000 ppm [NIOSH 1991]. The lowest lethal oral dose is estimated to be 14 mg/kg [NIOSH 1991]. Ingestion of the liquid produces corrosive tissue burns, mouth and esophageal pain, vomiting, diarrhea, shock (hypotension, tachycardia, cyanosis), headache, dizziness, delirium, collapse, and stupor. Death can result from glottic or pulmonary

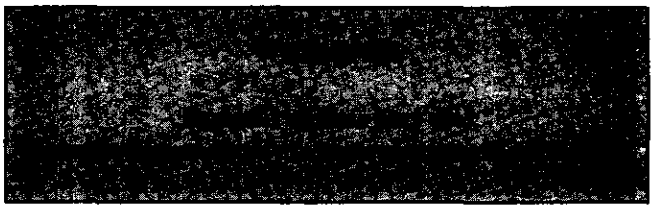
edema or aspiration pneumonia. Survivors can develop esophageal and pyloric stenoses [NLM 1992]. Regular exposure to 0.3 to 0.6 ppm for 1 year has induced headache, heart-area chest pain, irritability, anorexia, joint pain, and dyspepsia. Continued exposure for 5 to 6 years can cause loss of corneal reflexes, pharyngitis, vegetative disorders, thyroid hyperplasia and dysfunction, cardiovascular disorders (myocardial degeneration and hypotension), digestive tract secretory disorders, and inhibition of leucopoiesis and leucocytosis [NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to bromine can cause irritation or corrosion of contacted tissues, tearing, corneal clouding, dizziness, headache, pulmonary edema, dyspnea, nosebleeds, coughing, bronchopneumonia, central nervous system disturbances, abdominal pain, diarrhea, altered conditioned reflexes, delirium, collapse, and death. Survivors of ingestion incidents can develop esophageal and pyloric stenoses.

2. *Chronic exposure*: Chronic exposure to bromine can cause contact irritation, slow healing, painful acne-like skin eruptions, headache, heart pain, irritability, anorexia, joint pain, dyspepsia, loss of corneal reflexes, pharyngitis, vegetative disorders, thyroid dysfunction, and cardiovascular and digestive disorders.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of bromine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns and skin corrosion may result! ***Immediately*** remove contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of bromine are inhaled, move the victim to fresh air ***immediately***. If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if bromine or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve bromine and may result in worker exposures to this substance:

—Manufacture of ethylene dibromide, an anti-knock gasoline additive

—Use of bromine as a solvent

—Manufacture of pesticides

—Use of bromine in flame retardants for the plastics, fabric, and fiber industries

—Use of bromine as a sanitizing, disinfecting, bleaching, and water-purifying agent

—Manufacture of organic and inorganic compounds for use in photographic films and papers, sedatives, inks, anesthetics, hydraulic fluids, pharmaceuticals, fungicides, laboratory reagents, dyes and dyestuffs, war gases,

refrigerating and dehumidifying agents, and hair-waving preparations

—Use of bromine as a bleaching agent for silks and other fabrics, as a shrink-proofing agent for wool, as a desizing agent for cotton, and in gold extraction

The following methods are effective in controlling worker exposures to bromine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to bromine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to bromine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to bromine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromine on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for bromine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job

placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne bromine is determined by using a midget fritted-glass bubbler containing 10 ml of a standard eluent carbonate-bicarbonate solution (0.003 M $NaHCO_3$ to 0.0024 M Na_2CO_3). Samples are collected at a maximum flow rate of 0.5 liter/min until a recommended air volume of 30 liters is collected. (Sampling may continue up to a maximum volume of 120 liters.) Analysis is conducted by ion chromatography. The limit of detection for this procedure is 6.7 $\mu g/m^3$ for a 30-liter sample. This method is described in Method ID-108 of the *OSHA Analytical Methods Manual* [OSHA 1985]. An alternate method uses a silver membrane filter for sample collection, and ion chromatography for analysis with a limit of detection of 1.6 µg of bromine per sample. This method is described in Method 6011 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If bromine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then soak the affected areas in a 10% aqueous thiosulfate solution. Get medical help immediately.

Clothing and shoes contaminated with bromine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of bromine, particularly its potential for being corrosive to the eyes, skin, and respiratory tract.

A worker who handles bromine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where bromine or a solution containing bromine is handled, processed, or stored.

STORAGE

Bromine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of bromine should be protected from physical damage and should be stored separately from combustibles, organic or other readily oxidizable materials, ammonia, aluminum, titanium, mercury, potassium, alkali hydroxides, arsenites, ferrous and mercurous salts, hypophosphites, heat, sparks, direct sunlight, and open flame. Bromine should be stored at temperatures above −6.7°C (19.9°F) to prevent freezing; heating containers of bromine above atmospheric temperatures may rupture the containers. Because containers that formerly contained bromine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

Before bromine is handled in the workplace, an emergency plan for dealing with emergency spills or leaks of this substance must be developed. In the event of a spill or leak involving bromine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Stay upwind of the spill or leak area to the extent possible.

4. Neutralize small liquid spills by pouring a hypo solution (sodium thiosulfate or limewater) over them; the spilled material can then be absorbed with sand or other noncombustible absorbent material and placed in a covered container for later disposal.

5. Neutralize large liquid spills with a solution of potassium carbonate, sodium carbonate, or sodium bicarbonate; or build a dike far ahead of the spill to contain the bromine for later reclamation or disposal.

6. Neutralize bromine vapors in air by carefully releasing anhydrous ammonia gas (do ***not*** use aqueous ammonia gas).

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

If 500 lb or more of bromine is present at a facility, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for bromine is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although bromine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987c] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with bromine. Rubber boots, gloves, aprons, and full-body covering are recommended. Chemical protective clothing should be selected on the basis of available

performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon® has been tested against permeation by bromine and may provide good-to-excellent resistance for more than 4 but fewer than 8 hr. Polyethylene and natural rubber have been tested against bromine and have demonstrated poor resistance to permeation by bromine.

If bromine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which bromine might contact the eyes (e.g., through contact with the vapor or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with bromine. Contact lenses should not be worn if the potential exists for bromine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMINE PENTAFLUORIDE

INTRODUCTION

This guideline summarizes pertinent information about bromine pentafluoride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

BrF_5

- **Synonyms**

Bromine fluoride

- **Identifiers**

1. CAS No.: 7789-30-2
2. RTECS No.: EF9350000
3. DOT UN: 1745 44
4. DOT label: Oxidizer

- **Appearance and odor**

Bromine pentafluoride is a reactive, colorless or pale yellow, fuming liquid at temperatures below 40.3°C (104.5°F); it has a pungent odor and is not flammable. The odor threshold is unknown. At temperatures above 40.3°C (104.5°F), it is a colorless, pungent, and corrosive gas. It is shipped in compressed gas cylinders under its own vapor pressure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 174.92
2. Boiling point (760 mm Hg): 40.5°C (104.9°F)
3. Specific gravity (water = 1): 2.48 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of bromine pentafluoride): 6.05
5. Melting point: −60.5°C (−76.9°F)
6. Vapor pressure at 20°C (68°F): 328 mm Hg
7. Solubility: Reacts violently with water
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Bromine pentafluoride is stable under normal handling and storage procedures.

2. Incompatibilities: Bromine pentafluoride is a highly reactive compound; it reacts with every known element except the inert gases, nitrogen, and oxygen. Bromine pentafluoride is incompatible with acids, halogens, arsenic, selenium, alkaline halides, sulfur, iodine, glass, metallic halides, metal oxides, and metals (except copper, stainless steel, nickel, and Monel®). Fire or explosion may result from contact of bromine pentafluoride with combustibles or organic matter at room temperature, and contact of this substance with water produces an explosion.

3. Hazardous decomposition products: Toxic gases (such as hydrogen fluoride and hydrogen bromide) may be released in a fire involving bromine pentafluoride.

4. Special precautions: Even under mild reaction conditions, bromine pentafluoride attacks organic compounds vigorously, often causing an explosion.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to bromine pentafluoride.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable

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3. Flammable limits in air: Not applicable

4. Extinguishant: Avoid contact of this material with water. However, water may be used if large amounts of combustible material are involved in the fire and if firefighters can protect themselves by barriers or distance from the violent reaction of bromine pentafluoride and water. Fires involving bromine pentafluoride and small amounts of combustibles may be smothered using a carbon dioxide or dry chemical extinguishant.

Fires involving bromine pentafluoride should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of bromine pentafluoride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out; do **not** get water inside the containers. Stay away from the ends of containers. Runoff to sewers may create a fire or explosion hazard. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromine pentafluoride. Chemical protective clothing that is specifically recommended for bromine pentafluoride may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by bromine pentafluoride.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromine pentafluoride is 0.1 ppm (0.7 mg/m^3) as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.7 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromine pentafluoride a threshold limit value (TLV) of 0.1 ppm (0.7 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of irritation, corneal necrosis, and systemic effects associated with exposure to bromine pentafluoride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to bromine pentafluoride can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: Acute exposure to bromine pentafluoride is corrosive to the eyes, skin, mucous membranes, and upper respiratory tract, chronic exposure is toxic to the liver and kidneys. Experimental animals (species not identified) exposed to a 500-ppm concentration of bromine pentafluoride vapor immediately exhibited the following signs of acute distress: swollen eyelids, tearing, gasping, corneal cloudiness, and excessive salivation; reducing the concentration to 100 ppm produced these signs after an exposure of 3 min [ACGIH 1991a]. Exposure to 50 ppm caused death in these animals after 30 min [ACGIH 1991a]. At autopsy, animals chronically exposed to bromine pentafluoride at concentrations above 3 ppm showed toxic hepatosis and severe nephrosis, as well as severe respiratory involvement [ACGIH 1991a].

2. *Effects on Humans*: Bromine pentafluoride is a severe pulmonary irritant and is also intensely corrosive to the skin, eyes, and mucous membranes of humans in either the liquid or vapor state [Genium 1986]. Exposure to high (not further specified) concentrations are usually fatal; death is caused by respiratory damage and pulmonary edema [Braker and Mossman 1980]. Exposure to a concentration of 5 to 10 ppm is irritating to the eyes, nose, and throat; based on effects seen in animals, chronic exposure may cause liver, kidney, and lung damage [Braker and Mossman 1980; Genium 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to bromine pentafluoride can cause redness and tearing of the eyes, coughing, breathing difficulty, and a burning sensation of the eyes, nose, and throat. Direct contact of this substance with the eyes or skin can cause severe thermal and chemical burns and tissue destruction.

2. *Chronic exposure*: On the basis of effects seen in animals, long-term exposure to low levels of this substance may cause pain in the abdomen; enlargement of the liver;

blood, pus, or protein in the urine; jaundice; and other signs of lung, liver, or kidney damage.

- **Emergency procedures**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of bromine pentafluoride! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of bromine pentafluoride are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if bromine pentafluoride or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of bromine pentafluoride may result in worker exposures to this substance:

—Use as an oxidizer in liquid rocket propellant combinations and in chemical synthesis

—Use as a fluorinating agent in isotope enrichment and in fuel-element reprocessing

The following methods are effective in controlling worker exposures to bromine pentafluoride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers

for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to bromine pentafluoride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and lungs. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to bromine pentafluoride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with liver, kidney, or lung diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to bromine pentafluoride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromine pentafluoride on the liver, kidneys, and lungs. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for bromine pentafluoride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to bromine pentafluoride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne bromine pentafluoride is determined by using a silica gel tube (Supelco ORBO 53 or equivalent). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 48 liters is collected. Analysis is conducted by ion chromatography. This method is included in the *OSHA Chemical Information Manual* [OSHA 1987] and is based on OSHA Method ID-108.

PERSONAL HYGIENE

If bromine pentafluoride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water. Washing should be continued until the liquid is completely removed from the skin. The burned area should then be immersed in an ice bath, or a cold compress should be applied to the affected area.

Clothing and shoes contaminated with bromine pentafluoride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of bromine pentafluoride, particularly its potential for being corrosive to the skin and eyes.

A worker who handles bromine pentafluoride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where bromine pentafluoride is handled, processed, or stored.

STORAGE

Bromine pentafluoride should be isolated from other stored materials; it must be stored in a cool, dry, well-ventilated area in tightly sealed gas cylinders that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Extreme caution should be used when handling this material. Containers of bromine pentafluoride should be protected from physical damage and separated from combustible or organic materials, water, acids, halogens, arsenic, selenium, alkaline halides, sulfur, iodine, glass, metallic halides, metal oxides, metals (except for copper, stainless steel, nickel, and Monel), heat, sparks, and open flame. Bromine pentafluoride reacts with every known element except nitrogen, oxygen, and the inert gases. Because containers that formerly held bromine pentafluoride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving bromine pentafluoride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Remove leaking cylinder(s) to a safe place if feasible; attempt to stop the leak if it is possible to do so without risk.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Bromine pentafluoride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of bromine pentafluoride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromine pentafluoride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although bromine pentafluoride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromine pentafluoride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators

that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with bromine pentafluoride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to bromine pentafluoride permeation; however, sources recommend the use of acid suits, aprons, boots, neoprene gloves, and other appropriate protective clothing when handling this substance. Since specific test data are not available for bromine pentafluoride, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to bromine pentafluoride.

Safety glasses, goggles, or face shields should be worn during operations in which bromine pentafluoride might contact the eyes (e.g., through vapors or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with bromine pentafluoride. Contact lenses should not be worn if the potential exists for bromine pentafluoride exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BROMOFORM

INTRODUCTION

This guideline summarizes pertinent information about bromoform for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CHBr_3$

- **Synonyms**

Tribromomethane, methenyl tribromide, methyl tribromide

- **Identifiers**

1. CAS No.: 75-25-2
2. RTECS No.: PB5600000
3. DOT UN: 2515 58
4. DOT label: St. Andrew's Cross

- **Appearance and odor**

Bromoform is a nonflammable, colorless-to-dark-brown, fuming, volatile liquid with a suffocating chloroformlike odor; it may form hexagonal crystals at 6° to 7°C (43° to 45°F). The odor threshold is reported to be 1.3 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 252.8
2. Boiling point (at 760 mm Hg): 149° to 150°C (300.2° to 302°F)
3. Specific gravity (water = 1): 2.9 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of bromoform): 8.7
5. Melting point: 8.3°C (46.9°F)
6. Vapor pressure at 20°C (68°F): 5 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, benzene, chloroform, ether, petroleum ether, acetone, and oils
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Fires and explosions may result from contact of bromoform with chemically active metals (sodium, potassium, powdered aluminum, zinc, magnesium, lithium), calcium, acetone, or strong caustics (such as potassium hydroxide).
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide, bromine, hydrogen bromide, and bromine oxides) may be released in a fire involving bromoform.
4. Special precautions: Liquid bromoform attacks some coatings and some forms of plastic and rubber.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to bromoform; this substance is not flammable.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air (% by volume): Not applicable

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4. Extinguishant: Bromoform itself does not burn; use an extinguishant that is suitable for the material involved in the surrounding fire.

Fires involving bromoform should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving bromoform. Chemical protective clothing that is specifically recommended for bromoform may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by bromoform.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bromoform is 0.5 ppm (5 mg/m^3) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 ppm (5 mg/m^3) as an 8-hr TWA with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bromoform a threshold limit value (TLV) of 0.5 ppm (5.2 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a "Skin" notation [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of irritation and liver damage associated with exposure to bromoform.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to bromoform can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Bromoform is an irritant of the eyes, skin, and respiratory tract; a central nervous system depressant; and a liver and kidney toxin. The application of undiluted bromoform to the eyes of rabbits caused moderate irritation that healed within 1 or 2 days. Rabbits also acutely exposed dermally to undiluted bromoform (2,000 mg/kg) developed moderate skin irritation but did not die [Clayton and Clayton 1981]. Rabbits exposed to 1,070 to 1,270 ppm for an unspecified duration developed narcosis [Clayton and Clayton 1981]. A dog exposed for 1 hr to approximately 7,000 ppm experienced deep narcosis followed by death [ACGIH 1991a]. The oral LD_{50}s for male and female rats were 1,388 and 1,147 mg/kg, respectively. Exposure of rabbits to 243 ppm for 10 days resulted in functional changes in the central nervous system, liver, and kidneys plus vascular and dystrophic changes [Clayton and Clayton 1981]. Rats exposed to 24 ppm for 4 hr/day for 2 months developed disorders in liver prothrombin synthesis and glycogenesis as well as reduced renal filtration capacity [NLM 1991]. Bromoform was mutagenic when tested in three strains of *Salmonella typhimurium* [ACGIH 1991a]. Carcinogenicity bioassays were performed with mice and rats treated by gavage with various doses of bromoform for 5 days/week during 103 weeks. Although the male and female rats in these bioassays showed an increased incidence of adenomatous polyps or adenocarcinomas of the large intestine, the mice were unaffected by treatment [NTP 1989]. Mice given repeated intraperitoneal injections of bromoform developed a significantly increased incidence of pulmonary adenomas [Theiss et al. 1977].

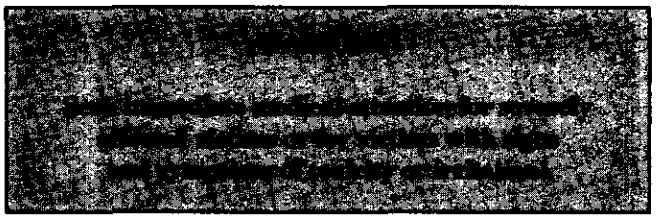
2. *Effects on Humans*: Bromoform has both narcotic and irritant effects in humans. Exposure to the vapor at unspecified concentrations causes irritation of the eyes, respiratory tract, pharnyx, and larnyx [Proctor et al. 1988]. Prolonged contact with the skin may lead to skin burns [NLM 1991]. Accidental ingestion of bromoform has produced central nervous system depression with coma and loss of reflexes; small doses have led to listlessness, headache, and vertigo [ACGIH 1991a].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to bromoform can cause irritation, tearing, headache, dizziness, vertigo, digestive symptoms, weight loss, excessive salivation, lethargy, sedation, amnesia, shock, convulsions, anesthesia, pulmonary edema, respiratory failure, and death.

2. *Chronic exposure*: No signs or symptoms of chronic bromoform exposure have been reported.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of bromoform. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of bromoform are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if bromoform or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of bromoform may result in worker exposures to this substance:

—Use as a reagent for graphite ore fractionation and as a heavy liquid flotation agent in mineral separation for sedimentary petrographical surveys, geological assays, and purification of materials such as quartz

—Use in the shipbuilding, aircraft, and aerospace industries

—Use as a solvent for waxes, greases, oils, and fats

—Use as an ingredient in fire-resistant chemicals and gauge fluids

—Use as an ingredient in pharmaceuticals and medicinal products such as antiseptics, sedatives, and cough suppressants

The following methods are effective in controlling worker exposures to bromoform, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to bromoform, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system, liver, kidneys, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to bromoform at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with central nervous system, liver, kidney, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to bromoform exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of bromoform on the central nervous system, liver, kidneys, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Inorganic bromide can be detected in the serum of bromine-exposed workers. Some sources suggest that the serum bromide concentration in bromoform-exposed workers should not exceed 15 to 30 mg/liter of serum. However, because few data correlate airborne exposure concentrations with serum bromide concentrations, no biological monitoring test acceptable for routine use has yet been developed for bromoform.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne bromoform is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then desorbed with carbon disulfide. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 5 μg per sample. This method is described in Method 1003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If bromoform contacts the skin, workers should flush the affected areas immediately with plenty of water and then wash thoroughly with soap and water.

Clothing contaminated with bromoform should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of bromoform, particularly its potential for causing eye and respiratory tract irritation.

A worker who handles bromoform should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where bromoform or solutions containing bromoform are handled, processed, or stored.

STORAGE

Bromoform should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of bromoform should be protected from physical damage and should be stored separately from caustic alkalies, chemically active metals (such as sodium, potassium, powdered aluminum, zinc, magnesium, and lithium), calcium, acetone, heat, sparks, and open flame. Because containers that formerly contained bromoform may hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving bromoform, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.

4. Absorb small spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

5. For large spills, build dikes far ahead of the spill to contain the bromoform for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Bromoform is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for bromoform is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of bromoform per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of bromoform emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Bromoform is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and it has been assigned EPA Hazardous Waste No. U225. Bromoform is approved for land disposal as long as the concentration of bromoform in the waste or treatment residual does not exceed 15 mg/kg. Bromoform also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of bromoform exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require

entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with bromoform. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by bromoform and have demonstrated protection for periods greater than 8 hr: polyvinyl alcohol and Viton®. Butyl rubber has demonstrated questionable resistance to permeation by bromoform. Natural rubber, neoprene, nitrile rubber, and polyvinyl chloride have demonstrated poor resistance to permeation by bromoform.

If bromoform is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which bromoform might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with bromoform. Contact lenses should not be worn if the potential exists for bromoform exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BUTADIENE (1,3-BUTADIENE)

INTRODUCTION

This guideline summarizes pertinent information about butadiene (1,3-butadiene) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_4H_6

- **Structure**

$CH_2=CH-CH=CH_2$

- **Synonyms**

1,3-Butadiene, trans-butadiene, bivinyl, divinyl, erythrene, vinylethylene, biethylene, butadiene monomer, pyrrolylene, 1-methylallene

- **Identifiers**

1. CAS No.: 106-99-0
2. RTECS No.: EI9275000
3. DOT UN: 1010 17 (inhibited butadiene)
4. DOT label: Flammable Gas (inhibited butadiene)

- **Appearance and odor**

Butadiene is a colorless, flammable gas with a mild aromatic odor. It is shipped under its own vapor pressure as a liquefied gas. The odor threshold is reported to be 1.1 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 54.1
2. Boiling point (760 mm Hg): -4.4°C (24°F)
3. Specific gravity (water = 1): 0.62 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of butadiene): 1.9
5. Melting point: -108.9°C (-164.0°F)
6. Vapor pressure at 21°C (69.8°F): 1,840 mm Hg
7. Solubility: Insoluble in water; soluble in alcohol, ether, acetone, and benzene
8. Evaporation rate: Not applicable; butadiene is a gas.

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, or open flame. When exposed to air, butadiene may form explosive peroxides.

2. Incompatibilities: Fires, explosions, or hazardous polymerization may result from contact of butadiene with air, strong oxidizers, ozone, nitrogen dioxide, copper, copper alloys, phenol, chlorine dioxide, crotonaldehyde, or a free radical polymerization initiator such as hydroquinone.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released in a fire involving butadiene.

4. Special precautions: Butadiene is self-reactive. To prevent hazardous polymerization, an inhibitor must be added to the butadiene and the concentration of inhibitor (such as tert-butylcatechol) must be monitored to ensure that it remains at effective levels at all times.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to butadiene.

1. Flash point: -156°F (105°C)
2. Autoignition temperature: 420°C (788°F)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Flammable limits in air (% by volume): Lower, 2.0; upper, 12.0

4. Extinguishant: Butadiene is a flammable gas. To extinguish a fire involving this substance, the flow of gas must be stopped. Fires involving butadiene should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of butadiene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving butadiene. Firefighters' protective clothing may not provide protection against permeation by butadiene.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for buta-diene is 1,000 ppm (2,200 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A]. However, OSHA has published a proposed rule on occupational exposure to butadiene that would reduce the PEL to 2 ppm as a TWA and 10 ppm as a short-term exposure limit (STEL) [55 FR 32736, August 10, 1990]. A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday.

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has recommended that butadiene be considered a potential occupational carcinogen and that exposure be limited to the lowest feasible concentration [NIOSH 1984a, 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated butadiene an A2 substance (suspected human carcinogen) and has assigned butadiene a threshold limit value (TLV) of 10 ppm (22 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The current OSHA limit is based on the risk of irritation and narcosis associated with exposure to butadiene and does not take into account the possible carcinogenic effects of this substance. The proposed OSHA PEL and NIOSH REL are based on butadiene's potential occupational carcinogenicity and reproductive toxicity. The ACGIH TLV is based on potential occupational carcinogenicity.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to butadiene can occur through inhalation and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: Butadiene is an irritant of the eyes and mucous membranes, and it is a narcotic at high concentrations. This substance is also a carcinogen and reproductive toxin in experimental animals. The 2-hr LC_{50} in rats is 270 g/m^3 (129,000 ppm) [NIOSH 1991]. Rabbits exposed for 8 to 10 min at 200,000 to 250,000 ppm were deeply anesthetized but recovered completely after exposure ceased. If the exposure was continued for 25 to 35 min, the animals died [ACGIH 1991a]. Inhalation of 625 or 1,250 ppm butadiene for 6 hr/day, 5 days/week for 6 weeks caused nonneoplastic effects in mice at several organ sites (ovaries, testes, nasopharynx, lung, and liver) [NIOSH 1984a]. Rats, guinea pigs, rabbits, and a dog exposed to butadiene concentrations ranging from 600 to 6,700 ppm for 7.5 hr/day, 6 days/week for 8 months developed no significant toxic effects [ACGIH 1991a; Proctor et al. 1988]. Inhalation exposure to butadiene at 200 ppm was toxic to pregnant rats and retarded embryonic growth and development; exposure at 8,000 ppm during pregnancy caused a significant increase in major skeletal abnormalities in the offspring [Proctor et al. 1988; ACGIH 1991a]. Butadiene has caused cancers in the mammary glands, uterus, ovaries, testes, thyroid gland, pancreas, liver, Zymbal gland, heart, lungs, lymph system, and hematopoietic system in rats and mice chronically exposed to this substance in inhalation bioassays [NIOSH 1984a]. On this basis, the International Agency for Research on Cancer (IARC) has concluded that butadiene is an animal carcinogen [IARC 1986].

2. *Effects on Humans*: Exposure to butadiene causes irritation of the eyes, mucous membranes, upper respiratory tract, and skin in exposed workers [Cralley and Cralley 1985; ACGIH 1991a]. Volunteers exposed to butadiene at 2,000 ppm experienced irritation of the eyes, nose, throat, and skin [NIOSH 1984a]. In contact with the skin, the liquid may cause frostbite [NIOSH 1984a]. Epidemiological studies of workers exposed to butadiene, styrene, and benzene at two styrene-butadiene rubber facilities (with average

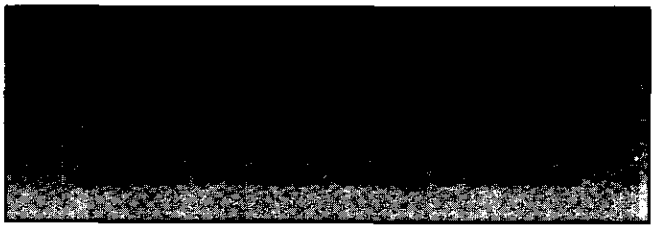
butadiene exposures of 1.24 and 13.5 ppm, respectively) have shown an increased, but not statistically significant, risk of mortality from lymphatic and hematopoietic system cancer and from leukemia [NIOSH 1984a]. IARC has stated that evidence is insufficient to conclude that butadiene is a human carcinogen [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to butadiene can cause irritation of the eyes, nose, and throat, with redness and tearing of the eyes, runny nose, and cough. Skin contact with butadiene in liquid form may cause burns or frostbite. At high concentrations, butadiene causes blurred vision, nausea, fatigue, headache, dizziness, rapid breathing, decreased blood pressure and pulse, diminished mental alertness, muscular incoordination, unconsciousness, respiratory paralysis, and death.

2. *Chronic exposure*: Prolonged or repeated skin contact with butadiene can induce dermatitis. On the basis of effects seen in animals, butadiene should be considered a potential carcinogen.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: If tissue is frozen, seek medical attention ***immediately***; if tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia persists, get medical attention as soon as possible.

2. *Skin exposure*: If frostbite has occurred, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If frostbite has ***not*** occurred, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve butadiene and may result in worker exposures to this substance:

—Manufacture of styrene-butadiene-rubber (SBR) elastomer, polybutadiene elastomer, neoprene elastomer, nitrile elastomer, styrene-butadiene (SB) copolymer, and acrylonitrile-butadiene-styrene (ABS) resins, which are used as reinforcing and stiffening agents for rubbers

—Manufacture of high-impact polystyrene containing SBR/polybutadiene elastomer and of SBR foams

—Molding and vulcanizing operations that process synthetic rubber products from SBR

—Use of butadiene in latexes and resins to make carpet backing, paper coatings, high-impact-resistant pipes and parts for automobiles, appliances, business machines, telephones, and recreational vehicles

—Manufacture of tires, hoses, belts, gaskets, seals, and oil-resistant textile and paper products

—Manufacture of adiponitrile; cyclo-olefins; 1,4-hexadiene tetramethylene sulfone; tetrahydrophthalic anhydride; hexamethylenediamine; ethylidenenorbornene; and 1,5,9-cyclodecatriene

—Use of butadiene in the Diels-Alder condensation reaction for synthesis of compounds

—Use of butadiene in food wrappings, the latex paint industry, rocket fuels, pesticides, and fungicides

The following methods are effective in controlling worker exposures to butadiene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to acrylic acid, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrylic acid at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system or skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to butadiene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of butadiene on the respiratory tract and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for butadiene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to butadiene may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne butadiene is determined by using charcoal tubes (100/50-mg sections, 20/40 mesh) coated with 10% (w/w) 4-tert-butylcatechol. Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 3 liters is collected. The sample is then treated with carbon disulfide to extract the butadiene. Analysis is conducted by gas chromatography using a flame ionization detector. The standard analytical error for this procedure is 0.11. The OSHA method is described in the OSHA Computerized Information System [OSHA 1990] and in Method 56 of the *OSHA Analytical Methods Manual*

[OSHA 1985]. NIOSH has a similiar method for butadiene [NIOSH 1984b]. OSHA Method 56 is compared with NIOSH Method 1024 in the NIOSH comments on the proposed rule for 1,3-butadiene [NIOSH 1990].

PERSONAL HYGIENE

If liquid butadiene contacts the skin, frostbite may occur. Workers should flush the affected areas immediately with plenty of tepid water and then wrap the affected part in a warm dressing. Medical aid should be obtained immediately.

Clothing contaminated with liquid butadiene should be removed immediately.

A worker who handles butadiene cylinders should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where butadiene cylinders are handled, processed, or stored.

STORAGE

Butadiene should be stored in a cool, dry, well-ventilated area in tightly sealed and pressurized containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside, isolated, or detached storage is preferred; inside storage should be in a noncombustible location. Containers of butadiene should be stored upright and should not be stacked. Containers of butadiene should be protected from physical damage and should be stored separately from oxygen, chlorine, phenol, chlorine dioxide, crotonaldehyde, copper, copper alloys, oxidizers, heat, sparks, and open flame. The manufacturer's recommendations regarding shelf life, rotation of inventory, and monitoring of levels of inhibitor should be followed rigorously. Only nonsparking tools may be used to handle butadiene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained butadiene may hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving butadiene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. *Do not touch the spilled material.*
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Isolate the area until the gas has dispersed.
5. If butadiene gas is leaking, stop the flow of gas if it is possible to do so without risk.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Butadiene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of butadiene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of butadiene per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of butadiene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although butadiene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in

Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of butadiene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with butadiene. Protective gloves and clothing are recommended for workers handling this material. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by butadiene and have demonstrated good-to-excellent resistance for periods of greater than 8 hr: butyl rubber and Viton®. Natural rubber, neoprene, and polyvinyl chloride have demonstrated poor resistance to permeation by butadiene.

If butadiene is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which butadiene might contact the eyes (e.g., through splashes of the liquid). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with liquid butadiene. Contact lenses should not be worn if the potential exists for butadiene exposure.

REFERENCES CITED

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTANE

INTRODUCTION

This guideline summarizes pertinent information about n-butane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

C_4H_{10}

- **Structure**

$CH_3CH_2CH_2CH_3$

- **Synonyms**

Butane, butyl hydride, diethyl, liquefied petroleum gas, methylethylmethane

- **Identifiers**

1. CAS No.: 106-97-8
2. RTECS No.: EJ4200000
3. DOT UN: 1011 22
4. DOT label: Flammable Gas

- **Appearance and odor**

n-Butane is a colorless gas with no odor, although an odorant is sometimes added to the gas to provide warning of its presence. This gas is commercially available in several grades of purity and in various mixtures (with the isobutane isomer, propane, and/or pentane). n-Butane is usually shipped under pressure as a liquefied gas and is one of the major ingredients in bottled gas.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 58.1
2. Boiling point (760 mm Hg): −0.5°C (31.1°F)
3. Specific gravity (water = 1): 0.5788 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-butane): 2.07
5. Melting point: −138.4°C (−217.1°F)
6. Vapor pressure at 20°C (68°F): 1,557 mm Hg
7. Solubility: Soluble in water; very soluble in alcohol, ether, and chloroform
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fire and explosions may result from contact of n-butane with oxidizers. A mixture of n-butane and oxygen will explode on contact with nickel carbonyl in the 20° to 40°C (68° to 104°F) temperature range.
3. Hazardous decomposition products: Acrid smoke and fumes may be released when n-butane undergoes thermal oxidative decomposition.
4. Special precautions: Do not use n-butane around sparking motors or other nonexplosionproof equipment. Ground all lines and equipment used with n-butane.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to n-butane.

1. Flash point: −60°C (−76°F) (closed cup) (liquefied n-butane).
2. Autoignition temperature: 430°C (806°F)

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Division of Standards Development and Technology Transfer

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3. Flammable limits in air (% by volume): Lower, approximately 1.9; upper, approximately 8.4

4. Extinguishant: Stop flow of gas. Use water to keep fire-exposed containers cool and to protect persons effecting the shutoff. If a leak or spill has not ignited, water spray may be used to disperse the gas or vapor and to protect persons attempting to stop the leak.

Fires involving n-butane should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of n-butane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-butane.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butane is 800 ppm (1,900 mg/m^3) as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for n-butane of 800 ppm (1,900 mg/m^3) as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-butane a threshold limit value (TLV) of 800 ppm (1,900 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on drowsiness and the risk of narcosis associated with exposure to n-butane.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to n-butane can occur through inhalation or eye and skin contact.

• Summary of toxicology

1. *Effects on Animals*: Contact with liquid n-butane can cause frostbite. This gas is also an anesthetic and asphyxiant in animals at very high concentrations. Although n-butane was mildly to moderately irritating to rabbit skin, it did not produce ocular or respiratory tract irritation [NLM 1992]. However, direct tissue contact with liquid n-butane can cause frostbite [NLM 1992]. Anesthetized dogs concomitantly exposed to 5,000 ppm developed hemodynamic changes (decreased myocardial contractility, stroke volume, cardiac output, and left ventricular and aortic pressures) [Clayton and Clayton 1981]. Dogs exposed to 10,000 ppm for 2 hr or 200,000 ppm for 2 min were hypersensitized to epinephrine-induced ventricular fibrillation. Exposure of dogs to 150,000 to 900,000 ppm for 10 min also caused heart sensitization to epinephrine-induced arrhythmias [NLM 1992]. The anesthetic concentration for n-butane is 250,000 ppm in dogs [NLM 1992] and 220,000 ppm for 1 min or 130,000 ppm for 25 min in mice [Clayton and Clayton 1981]. The 30-min LC_{50} for mice is approximately 285,000 ppm, but the 15-min LC_{50} for rats is about 275,000 ppm [NLM 1992]. n-Butane was not mutagenic in the *Salmonella typhimurium* assay [NLM 1992].

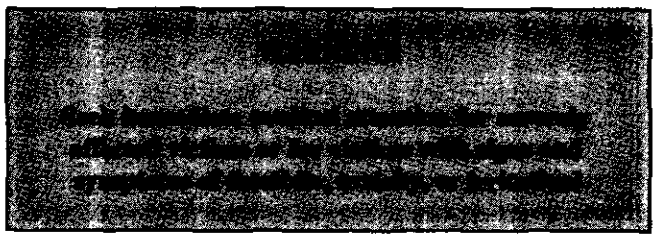
2. *Effects on Humans*: A transient blurring of vision resulted when n-butane was accidently sprayed into the eyes from a cigarette lighter [NLM 1992]. However, contact of the eyes or skin with n-butane gas does not normally cause irritation, but contact with the liquefied form may cause frostbite of the eyes or skin [Clayton and Clayton 1981; Genium 1990]. Exposure to 10,000 ppm for 10 min may lead to drowsiness but does not appear to cause systemic effects [Clayton and Clayton 1981]. A 2-year-old girl developed seizures, hypotension, and recurrent ventricular tachycardia following inhalation of an aerosol spray from a can containing a mixture of n-butane, isobutane, and propane [NLM 1992]. Progressive bilateral pulmonary infiltrates consistent with hydrocarbon pneumonitis developed in a "fire breather" following an inhalation of unignited fumes from a butane lighter. Exposure of volunteers to 1,000 ppm for 8 hr or 500 ppm for 8 hr/day, 5 days/week for 2 weeks did not induce toxicity [ACGIH 1991a]. Intentional inhalation abuse of n-butane for 1 year by a 16-year-old girl caused her to suffer from visual hallucinations, increased irritability, and social withdrawal [NLM 1992]. Exposure to n-butane at very high concentrations can affect the central nervous system, causing narcosis and asphyxiation [Clayton and Clayton 1981].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to n-butane can cause central nervous system depression (drowsiness and lightheadedness), narcosis, and asphyxiation. Contact with liquefied n-butane can cause eye and skin burns (frostbite).

2. *Chronic exposure*: Visual hallucinations, irritability, and social withdrawal have been reported with chronic exposure. Cardiac sensitization may also be possible.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: If tissue is frozen, seek medical attention ***immediately***; if tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the lower and upper eyelids. If irritation, pain, swelling, lacrimation, or photophobia persists, get medical attention as soon as possible.

2. *Skin exposure*: If frostbite has occurred, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If frostbite has ***not*** occurred, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve n-butane and may result in worker exposures to this substance:

—Use of n-butane as a raw material in the production of motor and aviation fuels

—Use of n-butane as a household fuel, solvent, refrigerant, standby and enricher gas, and propellant in aerosols

—Use of pure grades of n-butane in calibrating instruments

—Use of n-butane as a food additive

—Manufacture of ethylene and butadiene

—Use of n-butane as a special motor fuel for in-plant trucking, where the presence of gasoline vapors is undesirable

The following methods are effective in controlling worker exposures to n-butane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To

place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-butane.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-butane is determined by using two charcoal tubes in series (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the n-butane. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If liquefied n-butane contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and should not rub the affected areas.

Workers should not eat, drink, or use tobacco products in areas where n-butane is handled, processed, or stored.

Workers should wash their hands after handling liquefied n-butane.

STORAGE

n-Butane should be stored in a cool, dry, well-ventilated, low-fire-risk area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of n-butane should be protected from physical damage and should be stored separately from oxidizers (including cylinders of oxygen or chlorine), nickel carbonyl, heat, sparks, and open flame. All equipment used with n-butane should be electrically bonded and grounded. Because containers that formerly contained n-butane may still hold product residues, they should be handled appropriately.

LEAKS

In the event of a leak involving n-butane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate potentially explosive atmospheres; supply optimum explosionproof ventilation to disperse the gas.
4. Use self-contained breathing apparatus and protection against contact with the cold liquid to avoid frostbite when attempting to stop the leak.
5. Stop the leak or remove the leaky cylinder or tank to a safe, open area and vent it slowly to empty the container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Butane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of n-butane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-butane emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although n-butane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are

conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-butane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1900.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with n-butane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been shown to provide resistance to liquefied n-butane: neoprene rubber, the combination of nitrile and polyvinyl chloride, and Viton®. Natural rubber, nitrile, and polyvinyl chloride have demonstrated poor resistance to n-butane.

Safety glasses, goggles, or face shields should be worn during operations in which n-butane might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-butane. Contact lenses should not be worn if the potential exists for exposure to liquefied n-butane.

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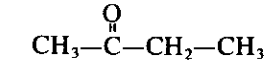
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-BUTANONE

INTRODUCTION

This guideline summarizes pertinent information about 2-butanone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_4H_8O
- **Structure:**



- **Synonyms:** Ethyl methyl ketone, MEK, methyl ethyl ketone
- **Identifiers:** CAS 78-93-3; RTECS EL6475000; DOT 1193, label required: "Flammable Liquid"
- **Appearance and odor:** Clear and colorless liquid with an odor like acetone

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 72.12
2. Boiling point (at 760 mmHg): 79.6 °C (175 °F)
3. Specific gravity (water = 1): 0.806
4. Vapor density (air = 1 at boiling point of 2-butanone): 2.5
5. Melting point: -86.5 °C (-123.7 °F)
6. Vapor pressure at 20 °C (68 °F): 70 mmHg; at 25 °C (77 °F), 100 mmHg
7. Solubility in water, g/100 g water at 20 °C (68 °F): 25.6
8. Evaporation rate (butyl acetate = 1): 5.7
9. Saturation concentration (approximate) at 20 °C (68 °F): 10.2 % (102,000 ppm); at 25 °C (77 °F), 13.2 % (132,000 ppm)
10. Ionization potential: 9.48 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., formaldehyde and carbon monoxide) may be released in a fire involving 2-butanone.

- **Flammability**

1. Flash point: -9 °C (16 °F) (closed cup)
2. Autoignition temperature: 515.5 °C (959 °F)
3. Flammable limits in air, % by volume: Lower, 2; upper, 10
4. Extinguishant: Carbon dioxide, dry chemicals, or alcohol foam
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 5 ppm
2. Eye irritation levels: 200-350 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, 2-butanone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-butanone is 200 parts of 2-butanone per million parts of air (ppm) [590 milligrams of 2-butanone per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 200 ppm (590 mg/m³) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 200 ppm (590 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 300 ppm (885 mg/m³) (Table 1).

Table 1.—Occupational exposure limits for 2-butanone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	200	590
NIOSH REL TWA	200	590
ACGIH TLV® TWA	200	590
STEL	300	885

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HEALTH HAZARD INFORMATION

• **Routes of exposure**

2-Butanone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**

Effects on animals: Acute inhalation of 2-butanone by guinea pigs caused narcosis, corneal opacities, emphysema, congestion of the brain, lungs, liver, and kidneys, and death. Inhalation of 2-butanone by pregnant rats caused an increased incidence of reduced lengths and weights in offspring.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 2-butanone can cause headache, dizziness, drowsiness, vomiting, and numbness of the extremities. Irritation of the eyes, nose, and throat can also occur.

2. *Long-term (chronic):* Exposure to 2-butanone can cause dryness and irritation of the skin.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to 2-butanone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to 2-butanone at or below the NIOSH REL (especially if exposure occurs in combination with 2-hexanone). The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis, a history of chronic skin disease, or a history and physical findings consistent with peripheral neuropathy.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to 2-butanone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

• **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to 2-butanone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to deter-

mine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting 2-butanone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure 2-butanone may also be used if available. A detailed sampling and analytical method for 2-butanone may be found in the *NIOSH Manual of Analytical Methods* (method number 2500).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with 2-butanone.

Workers should be provided with and required to use splash-proof goggles where 2-butanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with 2-butanone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-butanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-butanone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with 2-butanone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 2-butanone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 2-butanone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for 2-butanone

Operations	Controls
During spray application of vinyl and acrylic coatings; during mixing of dye solutions; during use in laboratories	Local exhaust ventilation, personal protective equipment
During surface spreading and coating of nitrocellulose and vinyl resins; during mixing, batching, and packaging of surface coating preparations; during forced drying of furniture finishes; during dewaxing; during use as a chemical intermediate	Local exhaust ventilation
During use in the application of adhesives for artificial leather	Dilution ventilation, personal protective equipment
During preparatory formulations of lacquers; during sponge or brush application of solvent for cleaning operations; during mixing of waterproofing compounds	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to 2-butanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-butanone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to 2-butanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-butanone gets on the skin, wash it immediately with soap and water. If 2-butanone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If 2-butanone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing 2-butanone, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from 2-butanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing 2-butanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. 2-Butanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing 2-butanone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for 2-butanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any powered air-purifying respirator with organic vapor cartridge(s) (substance causes eye irritation or damage—eye protection needed)
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Less than or equal to 3,000 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 3,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 200 ppm (590 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-BUTOXYETHANOL

INTRODUCTION

This guideline summarizes pertinent information about 2-butoxyethanol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{14}O_2$

- **Structure**

$CH_3(CH_2)_3OCH_2CH_2OH$

- **Synonyms**

2-Butoxy-1-ethanol; beta-butoxyethanol; o-butyl ethylene glycol; butyl glycol; butyl oxitol; ethylene glycol monobutyl ether; glycol butyl ether; monobutyl ether of ethylene glycol; n-butoxyethanol; Butyl Cellosolve; Dowanol EB; Ektasolve EB; Gafcol EB; Jeffersol EB; Poly-solv EB; EGBE

- **Identifiers**

1. CAS No.: 111-76-2
2. RTECS No.: KJ8575000
3. DOT UN: 2369 26
4. DOT labels: St. Andrew's Cross; Flammable Liquid

- **Appearance and odor**

2-Butoxyethanol is a clear, colorless liquid with a pleasant, etherlike odor. The odor threshold is reported to be 0.35 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 118.2
2. Boiling point (760 mm Hg): 171°C (340°F)
3. Specific gravity (water = 1): 0.90 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of 2-butoxyethanol): 4.1
5. Melting point: −70°C (−94°F)
6. Vapor pressure at 20°C (68°F): 0.8 mm Hg
7. Solubility: Miscible in water, alcohol, ether, mineral oil, and most organic solvents
8. Evaporation rate (butyl acetate = 1): 0.07

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of 2-butoxyethanol with strong oxidizers or caustics.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving 2-butoxyethanol.
4. Special precautions: 2-Butoxyethanol attacks some coatings and some forms of plastic and rubber; at high temperatures, this substance may attack metallic aluminum.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to 2-butoxyethanol.

1. Flash point: 62°C (143°F) (closed cup)
2. Autoignition temperature: 238°C (460°F)
3. Flammable limits in air (% by volume): Lower, 1.1 at 93°C (200°F); upper, 12.7 at 135°C (275°F)

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4. Extinguishant: Use alcohol foam, carbon dioxide, dry chemical, Halon®, water spray, or fog to fight fires involving 2-butoxyethanol. Do ***not*** use a solid stream of water because it will scatter and spread the fire.

Fires involving 2-butoxyethanol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of 2-butoxyethanol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving 2-butoxyethanol. Firefighters' protective clothing may not provide protection against permeation by 2-butoxyethanol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for 2-butoxyethanol is 25 ppm (120 mg/m3) as an 8-hr time-weighted average (TWA). The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (24 mg/m^3) as a 10-hr TWA for a 40-hr workweek; the REL also bears a "Skin" notation [NIOSH 1990, 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-butoxyethanol a threshold limit value (TLV) of 25 ppm (120 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 2-butoxyethanol [ACGIH 1991b].

• Rationale for limits

The OSHA and ACGIH limits are based on the risk of hematologic and other systemic effects associated with exposure to 2-butoxyethanol. The NIOSH limit is based on tissue irritation, CNS depression, and adverse effects of exposure on the blood and hematopoietic systems.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to 2-butoxyethanol can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: 2-Butoxyethanol is an irritant of the eyes, mucous membranes, and skin; it also causes hemolysis, kidney damage, reproductive effects, immunotoxicity, and embryotoxicity in animals. 2-Butoxyethanol caused severe corneal injury in rabbits [Tyler 1984]. When applied to the skin of rabbits for 4 hr, 2-butoxyethanol caused only mild irritation; extending the period of skin contact increased the degree of irritation [Tyler 1984]. Repeated application of this substance to rabbit skin caused systemic toxicity manifested as reduced body weight gain [Tyler 1984]. The oral LD_{50} is about 530 mg/kg in rats and 490 mg/kg in rabbits [NIOSH 1991]. At autopsy, acutely-poisoned animals exhibited kidney damage, narcotic effects, and breathing difficulty before death [Proctor et al. 1988]. Rats exposed to 245 ppm in air for 6 hr/day for 9 days showed significant depressions in red blood cell counts and hemoglobin concentrations and increases in nucleated erythrocytes, reticulocytes, and lymphocytes [Dodd et al. 1983]. Exposure of rats to 77 ppm in air for 30 hr/week for 90 days caused mild hematologic alterations. Fourteen days after exposure ceased, these hematologic effects were no longer evident [Dodd et al. 1983]. Male rats given 500 or 1,000 mg/kg per day for 4 days by oral gavage showed leukopenia and anemia; testicular atrophy was apparent in animals in the 500-mg/kg group [Grant et al. 1985]. Rats given 222, 443, or 885 mg/kg of 2-butoxyethanol by gavage for 6 weeks (5 days/week) showed a dose-dependent decrease in hemoglobin concentration and red blood cell count; these changes were apparent at all dose levels [Krasavage 1986; Ghanayem et al. 1990]. Teratogenicity studies have shown that 2-butoxyethanol to cause maternal, embryonic, and fetal toxicity in rats at 100 or 200 ppm, and maternal and embryonic toxicity in rabbits at 200 ppm [Tyl et al. 1984].

2. *Effects on Humans*: 2-Butoxyethanol is an irritant of the eyes and upper respiratory tract in humans. After an 8-hr exposure to 195 ppm, volunteers reported eye, nose, and throat discomfort; at 113 ppm for 4 hr, milder symptoms were experienced [Proctor et al. 1988]. Although humans appear to be less sensitive to the hematologic effects of 2-butoxyethanol than rats and mice, human red blood cells exposed in vitro showed increased fragility [Carpenter et al. 1956]. In one case report, a worker experienced two separate episodes of hematuria after being exposed to unspecified concentrations of 2-butoxyethanol and diethylene glycol monobutyl ether [Browning 1971].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to 2-butoxyethanol can cause irritation of the eyes, nose, and throat, with pain and tearing of the eyes, runny nose, and cough; skin irritation with redness and cracking; and narcotic effects with difficult breathing.

2. *Chronic exposure*: Chronic exposure to 2-butoxyethanol can cause dermatitis and hematuria.

- **Emergency procedures**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of 2-butoxyethanol. ***Immediately and thoroughly*** flush eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure*: If vapors, mists, or aerosols of 2-butoxyethanol are inhaled, move the victim to fresh air ***immediately***. If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if 2-butoxyethanol or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—*Induce vomiting* by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of 2-butoxyethanol may result in worker exposures to this substance:

—Use as a solvent for nitrocellulose resins and enamels, spray lacquers, quick-drying lacquers, varnishes, varnish removers, grease, oil, albumin, and dry cleaning compounds

—Use as a solvent for paints, printing inks, and dyestuffs and as an ingredient in agricultural chemicals, nonvolatile herbicides, brake oils, detergents for the automobile industry, penetrants, and softeners

—Use as a solvent for "soluble" mineral oils to hold soap in solution and to improve emulsifying properties

—Use as a solvent for protective coatings and metal cleaners

—Use as an agent to prevent spotting in textile printing and dyeing

—Use in production of acetate esters and phthalate and stearate plasticizers

—Use as a stabilizing agent in metal cleaners, textile lubricants, oils, hydraulic fluids, and liquid household cleaners

The following methods are effective in controlling worker exposures to 2-butoxyethanol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-butoxyethanol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, kidneys, liver, respiratory system, and blood. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-butoxyethanol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin, kidney, liver, respiratory system, or blood diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-butoxyethanol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-butoxyethanol on the skin, kidney, liver, respiratory system, and blood. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although butoxy acetic acid (BAA), a metabolite of 2-butoxyethanol, can be detected in the urine of exposed individuals, excreted levels of butoxy acetic acid do not correlate with airborne concentrations of 2-butoxyethanol. Therefore, no biological monitoring test acceptable for routine use has yet been developed for

2-butoxyethanol. However, NIOSH has recommended guidelines for biological monitoring of BAA [NIOSH 1990].

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne 2-butoxyethanol is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with methylene chloride/methanol (95:5) to extract the 2-butoxyethanol. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 to 0.02 mg per sample. This method is described in Method 1403 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984]. A similar method for sampling and analyzing 2-butoxyethanol is included in Method 83 of the *OSHA Analytical Methods Manual* [OSHA 1990].

PERSONAL HYGIENE

2-Butoxyethanol can be absorbed through the skin in toxic amounts. Therefore, if 2-butoxyethanol contacts the skin, workers should immediately flush the skin with large amounts of water and then wash with soap and water.

Clothing and shoes contaminated with 2-butoxyethanol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of 2-butoxyethanol, particularly its potential for being absorbed through the skin in toxic amounts.

A worker who handles 2-butoxyethanol should thoroughly wash hands with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where 2-butoxyethanol is handled, processed, or stored.

STORAGE

2-Butoxyethanol should be stored in a cool, dry, dark, well-ventilated area in tightly sealed, resin-coated, stainless steel containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. This substance should not be stored in aluminum containers. Electrical service in the storage area must be of explosionproof design. Containers of 2-butoxyethanol should be protected from physical damage and should be stored separately from strong oxidizers, strong caustics, heat, sparks, and open flame. Only nonsparking tools should be used to handle this substance. To prevent static sparks, all containers and equipment used to transfer 2-butoxyethanol must be bonded and grounded. Because containers that formerly contained 2-butoxyethanol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-butoxyethanol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres with maximally explosionproof ventilation.

5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the 2-butoxyethanol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore

advised to determine periodically whether new information is available.

- **Emergency planning requirements**

2-Butoxyethanol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of 2-butoxyethanol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of 2-butoxyethanol emitted or released from their facility annually.

- ***Hazardous waste management requirements***

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although 2-butoxyethanol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- ***Conditions for respirator use***

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-butoxyethanol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with 2-butoxyethanol. Gloves, aprons, guantlets, boots, and other protective clothing should be worn as necessary. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Butyl rubber and Saranex® have been recommended for use against permeation by 2-butoxyethanol and may provide protection for periods greater than 8 hr. Natural rubber, polyvinyl alcohol, and polyvinyl chloride have demonstrated poor resistance to permeation by 2-butoxyethanol.

If 2-butoxyethanol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-butoxyethanol might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be

available within the immediate work area whenever the potential exists for eye or skin contact with 2-butoxyethanol. Contact lenses should not be worn if the potential exists for 2-butoxyethanol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL ACETATE

INTRODUCTION

This guideline summarizes pertinent information about n-butyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{12}O_2$

- **Structure**

$CH_3COO(CH_2)_3CH_3$

- **Synonyms**

n-Butyl acetate; butyl ethanoate; acetic acid, n-butyl ester; 1-butyl acetate

- **Identifiers**

1. CAS No.: 123-86-4
2. RTECS No.: AF7350000
3. DOT UN: 1123 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

n-Butyl acetate is a clear, colorless, flammable liquid with a fruity odor. The odor threshold is reported to be 0.7 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.2
2. *Boiling point (at 760 mm Hg)*: 126°C (258°F)
3. Specific gravity (water = 1): 0.88 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-butyl acetate): 4.0
5. Melting point: -77.9°C (-108.2°F)
6. Vapor pressure at 20°C (68°F): 10 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, ether, and most hydrocarbons
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires may result from contact of n-butyl acetate with potassium-tert-butoxide, nitrates, strong oxidizers, strong alkalies, and strong acids.
3. Hazardous decomposition products: Toxic gases and vapors (such as partial oxidation products, carbon dioxide, and carbon monoxide) may be released in a fire involving n-butyl acetate.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to n-butyl acetate.

1. Flash point: 22°C (72°F) (closed cup)
2. Autoignition temperature: 425°C (797°F)
3. Flammable limits in air (% by volume): Lower, 1.7; upper, 7.6
4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving n-butyl acetate. A stream of water should not be used to extinguish fires involving this substance because the water will scatter and spread the fire.

Fires involving n-butyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of n-butyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-butyl acetate. Firefighters' protective clothing may not provide protection against permeation by n-butyl acetate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butyl acetate is 150 ppm (710 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 200 ppm (950 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 150 ppm (710 mg/m^3) as an 8-hr TWA and 200 ppm (950 mg/m^3) as a STEL [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-butyl acetate a threshold limit value (TLV) of 150 ppm (713 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 200 ppm (950 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of sensory irritation associated with exposure to n-butyl acetate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to n-butyl acetate can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: n-Butyl acetate causes moderate to severe irritation of the eyes, skin, and upper respiratory tract in animals; at high concentrations, it can cause narcosis and death from respiratory failure. In rabbits, n-butyl acetate caused moderate skin irritation after 24 hr of exposure and severe eye irritation after instillation [NIOSH 1991]. Guinea pigs exposed to 3,300 ppm showed signs of eye irritation; exposure to 7,000 ppm for 11 hr caused narcosis [Proctor et al. 1988]. In rats, the oral LD_{50} is 14 g/kg, and the LC_{50} is 2,000 ppm for 4 hr [NIOSH 1991]. Nearly saturated vapor (10,000 ppm) was fatal to six rats following an 8-hr exposure. Mice exposed to n-butyl acetate at concentrations ranging from 3,100 to 4,200 ppm 6 hr/day for 6 days showed signs of fatigue, weight loss, and an increase in formed elements in the blood and in hemoglobin levels [NLM 1991]. When administered during pregnancy, n-butyl acetate was embryotoxic in mice and rats [NIOSH 1991; NLM 1991].

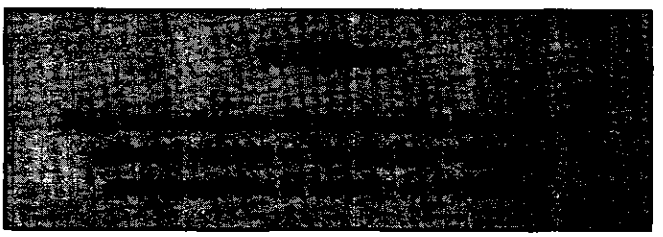
2. *Effects on Humans*: n-Butyl acetate is an irritant of the eyes, nose, respiratory tract, and skin in exposed workers. Volunteers exposed to n-butyl acetate at 200 ppm reported upper respiratory tract irritation; at 300 ppm, this irritation was reported to be severe [ACGIH 1991a]. Humans exposed to concentrations as high as 3,300 ppm experienced lacrimation and conjunctival redness [Grant 1986]. Vacuolar keratitis occurred in workers exposed to a mixture of butyl acetate and isobutyl alcohol. Hepatotoxicity has also been reported. Repeated skin contact with n-butyl acetate caused dermatitis in a pharmaceutical plant worker [NLM 1991].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to n-butyl acetate can cause contact irritation, headache, muscle weakness, giddiness, dizziness, ataxia, confusion, delirium, CNS and respiratory depression, coma, and death from respiratory failure.

2. *Chronic exposure*: Chronic exposure to n-butyl acetate can cause eye irritation and dryness, redness, scaling, and cracking of the skin.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of n-butyl acetate. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of n-butyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if n-butyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve n-butyl acetate and may result in worker exposures to this substance:

—Use of n-butyl acetate as a solvent and thinner for gums, oil, fats, waxes, pitch, lacquers, enamels, nitrocellulose, camphor, ethyl cellulose acetate, pyroxylin, chlorinated rubber, artificial leathers, ester-soluble dyes, airplane dopes, perfumes, natural gums, synthetic resins, and vinyl, polystyrene, and methacrylate plastics

—Application of nitrocellulose lacquers by spraying, brushing, or dipping and of surface coatings other than nitrocellulose lacquers, including paper coatings, lamp coatings, and airplane dope enamels

—Use of n-butyl acetate as a dehydrating agent

—Production of protective coatings in the automobile industry, flavorings, perfumes, safety glass, plastics, cosmetics, adhesives, shoe polishes, stain removers, photographic films, penicillin, and larvicides

The following methods are effective in controlling worker exposure to n-butyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to n-butyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to n-butyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to n-butyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of n-butyl acetate on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-butyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-butyl acetate is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide or carbon disulfide/dimethylformamide to extract the n-butyl acetate. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.02 mg per sample. This method is described in Method No. 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If n-butyl acetate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing contaminated with n-butyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of n-butyl acetate, particularly its potential to be irritating to the skin.

A worker who handles n-butyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where n-butyl acetate or a solution containing n-butyl acetate is handled, processed, or stored.

STORAGE

n-Butyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. This substance is an OSHA IB flammable liquid and must be handled accordingly. Containers of n-butyl acetate should be protected from physical damage

and should be stored separately from potassium tert-butoxide, strong oxidizers, nitrates, strong alkalies, strong acids, explosives, heat, sparks, open flame, and materials that are readily impregnable by odor. Only nonsparking tools may be used to handle n-butyl acetate. To prevent static sparks, containers and equipment should be grounded and bonded for transfers. Because containers that formerly contained n-butyl acetate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving n-butyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the n-butyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Butyl acetate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by EPA regulations resulting from the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for n-butyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Reponse Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-butyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although n-butyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of n-butyl acetate are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

• **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-butyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

• **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with n-butyl acetate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by n-butyl acetate and have demonstrated protection for more than 4 but fewer than 8 hr: polyvinyl alcohol, Teflon®, and polyethylene/ethylene vinyl alcohol. Butyl rubber has demonstrated questionable protection from permeation. Natural rubber, neoprene, nitrile rubber, polyethylene, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by n-butyl acetate.

If n-butyl acetate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which n-butyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-butyl acetate. Contact lenses should not be worn if the potential exists for n-butyl acetate exposure.

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ACGIH [1991a]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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NLM [1991]. The hazardous substances data bank: n-butyl acetate. Bethesda, MD: National Library of Medicine.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE

FOR sec-BUTYL ACETATE

INTRODUCTION

This guideline summarizes pertinent information about sec-butyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{12}O_2$

- **Structure**

$CH_3COOCH(CH_3)(C_2H_5)$

- **Synonyms**

Acetic acid, 1-methylpropyl ester; acetic acid, 2-butoxy ester; sec-butyl alcohol acetate; acetic acid, sec-butyl ester; 2-butyl acetate; 1-methylpropylacetate; 2-butanol acetate; acetic acid, secondary butyl ester

- **Identifiers**

1. CAS No.: 105-46-4
2. RTECS No.: AF7380000
3. DOT UN: 1123 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

sec-Butyl acetate is a flammable, colorless liquid with a mild fruity odor. The odor threshold is reported to be below 200 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.2
2. Boiling point (at 760 mm Hg): 112°C (233.6°F)
3. Specific gravity (water = 1): 0.88 at 16°C (60.8°F)
4. Vapor density (air = 1 at boiling point of sec-butyl acetate): 4.0
5. Melting point: −99°C (−146°F)
6. Vapor pressure at 20°C (68°F): 10 mm Hg
7. Solubility: Slightly soluble in water; miscible with common solvents
8. Evaporation rate (butyl acetate = 1): 2.0

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of sec-butyl acetate with nitrates, strong oxidizers, strong alkalies, or strong acids.
3. Hazardous decomposition products: Toxic gases and particulates (such as carbon monoxide, acrid smoke, and irritating fumes) may be released when sec-butyl acetate decomposes.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to sec-butyl acetate.

1. Flash point: 31°C (88°F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air (% by volume): Lower, 1.7; upper, 9.8

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

4. Extinguishant: Use alcohol foam, carbon dioxide, dry chemical, or Halon® to fight fires involving sec-butyl acetate. Water may be ineffective for extinguishing fires, but it may be used to cool fire-exposed containers.

Fires involving sec-butyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of sec-butyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving sec-butyl acetate. Firefighters' protective clothing may not provide protection against permeation by sec-butyl acetate.

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for sec-butyl acetate is 200 ppm (950 mg/m^3) as an 8-hr time-weighted average (TWA) [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 200 ppm (950 mg/m^3) as an 8-hr TWA [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned sec-butyl acetate a threshold limit value (TLV) of 200 ppm (950 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• **Rationale for limits**

The limits are based on the risk of eye and upper respiratory tract irritation associated with exposure to sec-butyl acetate.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to sec-butyl acetate can occur through inhalation, ingestion, and eye or skin contact.

• **Summary of toxicology**

1. *Effects on Animals*: sec-Butyl acetate is an irritant of the eyes, skin, and upper respiratory tract. On the basis of effects seen in animals exposed to other acetates, it is likely that sec-butyl acetate will cause narcosis in animals exposed to high concentrations [Proctor et al. 1988].

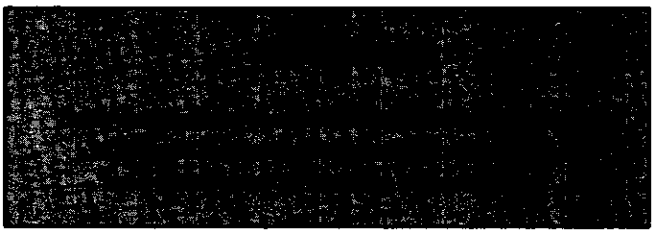
2. *Effects on Humans*: sec-Butyl acetate is an irritant of the eyes and upper respiratory tract. Based on effects seen in humans exposed to chemically similar substances, sec-butyl acetate is likely to cause narcosis at high concentrations [Proctor et al. 1988].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to sec-butyl acetate can cause redness and tearing of the eyes, runny nose, and sore throat. In contact with the skin, sec-butyl acetate may cause redness, defatting, and cracking. At high concentrations, workers may experience headache, fatigue, drowsiness, dizziness, or other symptoms of central nervous system depression and narcosis.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to sec-butyl acetate have been reported; however, prolonged exposure may increase the severity of the acute dermal effects noted above.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of sec-butyl acetate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of sec-butyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if sec-butyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of sec-butyl acetate may result in worker exposures to this substance:

—Use as a general solvent

—Use as a solvent for nitrocellulose, artificial leather, thinners, and nail enamels

The following methods are effective in controlling worker exposures to sec-butyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to sec-butyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to sec-butyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable

medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to sec-butyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of sec-butyl acetate on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for sec-butyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne sec-butyl acetate is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the sec-butyl acetate. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.2 mg/sample. This method is described in Method 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If sec-butyl acetate contacts skin, workers should wash the affected areas with soap and water.

Clothing and shoes contaminated with sec-butyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of sec-butyl acetate, particularly its potential for irritating the skin.

A worker who handles sec-butyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where sec-butyl acetate or a solution containing it is handled, processed, or stored.

STORAGE

sec-Butyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Electrical service in the storage area must meet requirements for an OSHA Class IB flammable liquid. To prevent static sparks, containers of sec-butyl acetate must be grounded and bonded. Containers also should be protected from physical damage and should be stored separately from direct sunlight, nitrates, strong oxidizers, strong alkalies, strong acids, heat, sparks, and open flames. Drums used to store sec-butyl acetate must be equipped with self-closing valves, pressure-vacuum bungs, and flame arresters. Only nonsparking tools may be used to transfer or handle sec-butyl acetate. Because containers that formerly contained sec-butyl acetate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving sec-butyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the sec-butyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

sec-Butyl acetate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.4] to notify the proper Federal, State, and local authorities.

The reportable quantity for sec-butyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of sec-butyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although sec-butyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of sec-butyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator*

Decision Logic [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with sec-butyl acetate. Gloves, aprons, and other protective clothing are recommended as necessary. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material is recommended for use against permeation by sec-butyl acetate: polyvinyl alcohol.

If sec-butyl acetate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which sec-butyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with sec-butyl acetate. Contact lenses should not be worn if the potential exists for sec-butyl acetate exposure.

REFERENCES CITED

ACGIH [1991a]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE

FOR tert-BUTYL ACETATE

INTRODUCTION

This guideline summarizes pertinent information about tert-butyl acetate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{12}O_2$

- **Structure**

$CH_3COOC(CH_3)_3$

- **Synonyms**

t-Butyl acetate; acetic acid, tert-butyl ester; acetic acid, 1,1-dimethyl ethyl ester; Texaco Lead Appreciator; TLA

- **Identifiers**

1. CAS No.: 540-88-5
2. RTECS No.: AF7400000
3. DOT UN: 1123 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

tert-Butyl acetate is a flammable, colorless liquid with a fruity odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.2
2. Boiling point (at 760 mm Hg): 97° to 98°C (206.6° to 208.4°F)
3. Specific gravity (water = 1): 0.87 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of tert-butyl acetate): 4.0
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): Data not available
7. Solubility: Insoluble in water; soluble in alcohol and ether
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fire and explosions may result from contact of tert-butyl acetate with nitrates, strong oxidizers, strong alkalies, and strong acids.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving tert-butyl acetate.
4. Special precautions: tert-Butyl acetate may soften or dissolve plastics.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to tert-butyl acetate; however, other sources rate this substance's fire hazard potential as severe.

1. Flash point: Between 16.6° and 22°C (62° and 72°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air (% by volume): Lower, 1.5; upper, data not available

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4. Extinguishant: Use alcohol foam, carbon dioxide, dry chemical, water spray, or Halon® to fight fires involving tert-butyl acetate.

Fires involving tert-butyl acetate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of tert-butyl acetate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing, including a self-contained breathing apparatus, when fighting fires involving tert-butyl acetate. Firefighters' protective clothing may not provide protection against permeation by tert-butyl acetate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for tert-butyl acetate is 200 ppm (950 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 200 ppm (950 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned tert-butyl acetate a threshold limit value (TLV) of 200 ppm (950 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991a].

- **Rationale for limits**

The limits are based on the risk of eye and respiratory tract irritation associated with exposure to tert-butyl acetate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to tert-butyl acetate can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals*: tert-Butyl acetate has not been tested for toxicity in animals. However, by analogy with the effects of other acetate esters, tert-butyl acetate is likely to cause eye, nose, and skin irritation and, at high concentrations, narcosis [Proctor et al. 1988].

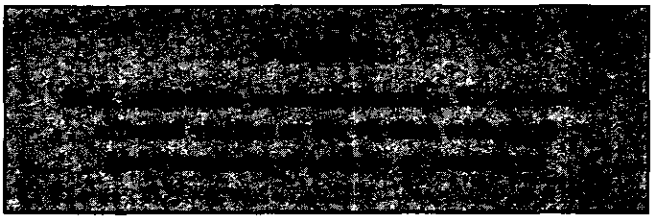
2. *Effects on Humans*: Exposure to tert-butyl acetate causes eye, skin, and respiratory irritation in workers. By analogy with the effects of similar esters, tert-butyl acetate is likely to cause narcosis at high concentrations [ACGIH 1991a].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to tert-butyl acetate can cause itchy or inflamed eyes and irritation of the nose and upper respiratory tract. Exposure to high concentrations of tert-butyl acetate may cause headache, drowsiness, and other narcotic effects.

2. *Chronic exposure*: No chronic effects of exposure to tert-butyl acetate have been reported; however, prolonged exposure may increase the severity of the acute dermal effects noted above.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of tert-butyl acetate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of tert-butyl acetate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if tert-butyl acetate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of tert-butyl acetate may result in worker exposures to this substance:

—Use as a solvent

—Use as an additive to improve the antiknock properties of motor fuels

The following methods are effective in controlling worker exposures to tert-butyl acetate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to tert-butyl acetate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to tert-butyl acetate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced

occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to tert-butyl acetate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of tert-butyl acetate on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for tert-butyl acetate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne tert-butyl acetate is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then desorbed with carbon disulfide. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.02 mg per sample. This method is described in Method 1450 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If tert-butyl acetate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing contaminated with tert-butyl acetate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of tert-butyl acetate, particularly its potential to be irritating to the eyes and skin.

A worker who handles tert-butyl acetate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where tert-butyl acetate is handled, processed, or stored.

STORAGE

tert-Butyl acetate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of tert-butyl acetate should be protected from physical damage and should be stored separately from nitrates, strong oxidizers, strong acids, strong alkalies, heat, sparks, and open flame. Because containers that formerly contained tert-butyl acetate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a leak involving tert-butyl acetate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors, but be aware that the spray may not prevent ignition in closed spaces.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the tert-butyl acetate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

tert-Butyl acetate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for tert-butyl acetate is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of tert-butyl acetate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although tert-butyl acetate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of tert-butyl acetate are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of tert-butyl acetate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with tert-butyl acetate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to permeation by tert-butyl acetate; however, the following materials have been tested against permeation by a chemically similar substance (n-butyl acetate) and have demonstrated protection for more than 4 but fewer than 8 hr: polyvinyl alcohol, polyethylene/ethylene vinyl alcohol, and Teflon®. Natural rubber, neoprene, nitrile rubber,

polyethylene, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by n-butyl acetate. Since specific test data are not available for tert-butyl acetate, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to tert-butyl acetate.

If tert-butyl acetate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which tert-butyl acetate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with tert-butyl acetate. Contact lenses should not be worn if the potential exists for tert-butyl acetate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BUTYL ACRYLATE

INTRODUCTION

This guideline summarizes pertinent information about butyl acrylate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_7H_{12}O_2$

- **Structure**

$CH_2 = CHCOOC_4H_9$

- **Synonyms**

2-Propenoic acid, butyl ester; acrylic acid, butyl ester; acrylic acid, n-butyl ester; butyl 2-propenoate

- **Identifiers**

1. CAS No.: 141-32-2
2. RTECS No.: UD3150000
3. DOT UN: 2348 26 (for the inhibited form)
4. DOT label: Flammable Liquid

- **Appearance and odor**

Butyl acrylate is a flammable, clear, colorless liquid with a sharp, fragrant, characteristic odor. The odor threshold is reported to be 0.1 part per billion (ppb) parts of air. Butyl acrylate is highly reactive and can undergo spontaneous polymerization. To prevent premature polymerization, the commercially available product often contains an inhibitor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 128.17
2. Boiling point (760 mm Hg): 145°C (293°F) (polymerizes)
3. Specific gravity (water = 1): 0.9 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of butyl acrylate): 4.4
5. Melting point: -64°C (-83.2°F)
6. Vapor pressure at 20°C (68°F): 4 mm Hg
7. Solubility: Very slightly soluble in water; soluble in alcohol, ether, and acetone.
8. Evaporation rate (butyl acetate = 1): 0.42

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame (heat may cause an explosive polymerization reaction)
2. Incompatibilities: Hazardous polymerization may result from contact of butyl acrylate with peroxides, sunlight, or other catalysts. Butyl acrylate is incompatible with strong acids, strong alkalies, amines, halogens, hydrogen compounds, and oxidizers.
3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and carbon monoxide) may be released in a fire involving butyl acrylate.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to butyl acrylate.

1. Flash point: 49°C (120°F) (open cup)
2. Autoignition temperature: 293°C (559°F)
3. Flammable limits in air (% by volume): Lower, 1.4; upper, 9.9

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4. Extinguishant: Use dry chemical, foam, or carbon dioxide to fight fires involving butyl acrylate. Water may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving butyl acrylate should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of butyl acrylate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving butyl acrylate. Firefighters' protective clothing may not provide protection against permeation by butyl acrylate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for butyl acrylate is 10 ppm (55 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (55 mg/m^3) as an 8-hr TWA [NIOSH 1992].

- **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned butyl acrylate a threshold limit value (TLV) of 10 ppm (52 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

- **Rationale for limits**

The limits are based on the risk of eye and skin irritation associated with exposure to butyl acrylate and on its toxicological similarity to methyl acrylate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to butyl acrylate can occur through inhalation, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals*: Butyl acrylate is an irritant of the eyes, skin, and respiratory tract in animals. Instillation of this substance into the eyes of rabbits also caused mild to moderate irritation [NIOSH 1991]. Corneal necrosis occurred when ocular washing was not performed [ACGIH 1991a]. When applied to the skin of rabbits for 24 hr, 10 mg butyl acrylate caused mild irritation. Butyl acrylate is a sensitizer in guinea pigs, and sensitized animals showed cross-sensitization reactions to other monoacrylates [IARC 1986]. The dermal LD_{50} for rabbits has ranged from 1,800 to 3,000 mg/kg [Carpenter et al. 1974; Smyth et al. 1951]. The maximum duration that all rats survived exposure to inhalation of saturated vapors (7,050 ppm) was 30 min [ACGIH 1991a; Smyth et al. 1951]. The 2-hr LC_{50} is 1,345 ppm for mice and 6,035 ppm for rats [Izmerov et al. 1982]. The 4-hr LC_{50} in rats is 2,730 ppm [NIOSH 1991]. These animals exhibited signs of eye and respiratory tract irritation (e.g., corneal necrosis and labored breathing) [ACGIH 1991a; Proctor et al. 1988]. Wide variations are reported in the oral LD_{50} for rats: 900 mg/kg [Izmerov et al. 1982]; 3,730 mg/kg [Smyth et al. 1951]; and 8,050 mg/kg [Carpenter et al. 1974]. The oral LD_{50} in mice has ranged from 5,400 to 7,500 mg/kg [IARC 1986]. Rats were exposed for 6 hr/day to 25, 135, or 250 ppm on days 6 to 15 after mating. Maternal toxicity and embryo lethality occurred at the two highest doses, but exposure to 25 ppm caused no observable effects. However, terata were not induced by any concentration of butyl acrylate [Proctor et al. 1988]. The International Agency for Research on Cancer (IARC) found no evidence of mutagenic potential in the in vivo or in vitro data reviewed [IARC 1986]. In a dermal carcinogenesis study, 1% butyl acrylate in acetone was applied three times weekly to the skin of mice over their lifetimes; no site-of-application tumors occurred in these animals [Proctor et al. 1988]. In a 2-year inhalation study, Sprague-Dawley rats were exposed to butyl acrylate concentrations ranging from 15 to 135 ppm. Exposures were for 6 hr/day, 5 days/week for 24 months followed by a 6-month recovery period. No tumors were induced by butyl acrylate after either the treatment or recovery periods [IARC 1986]. IARC has concluded that there is inadequate evidence of the carcinogenicity of butyl acrylate in animals [IARC 1986].

2. *Effects on Humans*: Butyl acrylate is an irritant of the eyes and skin as well as the mucous membranes of the nose, throat, and respiratory tract in humans [Gosselin et al. 1984]. Allergic contact dermatitis attributed to butyl acrylate has

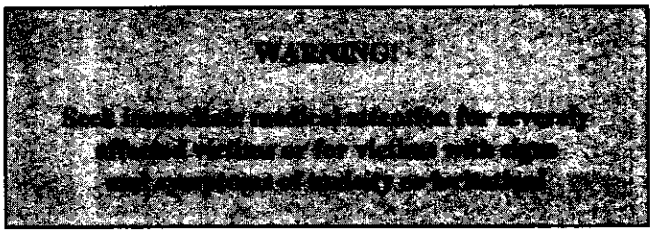
been reported in dentists, dental technicians, paint stock room clerks, and other occupationally exposed individuals [Kanerva et al. 1988; Proctor et al. 1988]. Fourteen of 33 workers exposed to 50 mg/m^3 (approximately 10 ppm) for an average of 5 years reported experiencing nervous system and behavioral symptoms, but these were not confirmed by electroencephalography [IARC 1986]. IARC classified butyl acrylate as a Group 3 material (not classifiable as to its carcinogenicity to humans) [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to butyl acrylate vapor can cause redness, tearing, and irritation of the eyes, runny nose, scratchy throat, difficult breathing, and redness and cracking of the skin.

2. *Chronic exposure*: Repeated contact of the skin with this substance may cause skin sensitization in some individuals, with redness, swelling, itching, and oozing of the affected areas. Nervous system and behavioral effects are also possible.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of butyl acrylate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of butyl acrylate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if butyl acrylate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve butyl acrylate and may result in worker exposures to this substance:

—Manufacture of polymers and resins for leather finishes, paint formulations, and textiles

—Organic synthesis of polymers and copolymers for solvent coatings, paper, adhesives, binders, sealants, and emulsifiers

The following methods are effective in controlling worker exposures to butyl acrylate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to butyl acrylate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to butyl acrylate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies or other findings consistent with skin or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to butyl acrylate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of butyl acrylate on the skin and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for butyl acrylate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne butyl acrylate is determined by using two XAD-2 tubes in series (80/50-mg sections, 20/50 mesh). Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 3 liters is collected. The sample is then treated with carbon disulfide to extract the butyl acrylate. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If butyl acrylate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with butyl acrylate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of butyl acrylate, particularly its potential for causing skin irritation and sensitization.

A worker who handles butyl acrylate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where butyl acrylate or a solution containing butyl acrylate is handled, processed, or stored.

STORAGE

Butyl acrylate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The inhibitor concentration in containers of this substance should be checked at regular intervals and inhibitor should be added as needed. Butyl acrylate should be stored at temperatures below 38°C (100°F). Containers of butyl acrylate should be protected from physical damage and should be stored separately from peroxides, strong acids, strong alkalies, amines, halogens, hydrogen compounds, oxidizers, sunlight, heat, sparks, and open flame. Because containers that formerly contained butyl acrylate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving butyl acrylate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the butyl acrylate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Butyl acrylate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of butyl acrylate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of butyl acrylate per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of butyl acrylate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although butyl acrylate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of

respirators to control exposure. Respirators must be worn if the ambient concentration of butyl acrylate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with butyl acrylate; impervious gloves are recommended. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon® has been tested against permeation by butyl acrylate and has demonstrated good-to-excellent resistance for more than 4 but fewer than 8 hr. Butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by butyl acrylate.

If butyl acrylate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which butyl acrylate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with butyl acrylate. Contact lenses should not be worn if the potential exists for butyl acrylate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about n-butyl alcohol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{10}O$

- **Structure**

$CH_3CH_2CH_2CH_2OH$

- **Synonyms**

1-Butanol, n-butanol, n-propyl carbinol, NBA, butyl hydroxide, butyric alcohol, normal primary butyl alcohol, methylal propane, propylmethanal, 1-hydroxybutane

- **Identifiers**

1. CAS No.: 71-36-3
2. RTECS No.: EO1400000
3. DOT UN: 1120 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

n-Butyl alcohol is a flammable, colorless liquid with a mild, wine-like odor. The odor threshold is reported to be between 0.12 and 11.0 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (at 760 mm Hg): 117° to 118°C (243° to 244°F)
3. Specific gravity (water = 1): 0.81 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-butyl alcohol): 2.6
5. Melting point: −90°C (−130°F)
6. Vapor pressure at 20°C (68°F): 6 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol, ether, and many other organic solvents
8. Evaporation rate (butyl acetate = 1): 0.46

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of n-butyl alcohol with strong oxidizers, strong mineral acids, alkali metals, or halogens.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving n-butyl alcohol.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to n-butyl alcohol.

1. Flash point: 37°C (98°F) (closed cup)
2. Autoignition temperature: 343°C (650°F)
3. Flammable limits in air (% by volume): Lower, 1.4; upper, 11.3
4. Extinguishant: Use carbon dioxide, dry chemical, or alcohol foam to fight fires involving n-butyl alcohol. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving n-butyl alcohol should be fought upwind and from the maximum distance possible. Isolate the hazard area

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and should ventilate closed spaces before entering. Containers of n-butyl alcohol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-butyl alcohol. Firefighters' protective clothing may not provide protection against permeation by n-butyl alcohol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butyl alcohol is 50 ppm (150 mg/m^3) as a ceiling limit. A worker's exposure to n-butyl alcohol shall at no time exceed this limit. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 50 ppm (150 mg/m^3) as a ceiling limit with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-butyl alcohol a ceiling limit of 50 ppm (152 mg/m^3), which should not be exceeded during any part of the working exposure. The ACGIH has also assigned n-butyl alcohol a "Skin" notation [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of possible vestibular and auditory nerve injury as well as headaches and irritation associated with exposure to n-butyl alcohol.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to n-butyl alcohol can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: n-Butyl alcohol is an irritant of the eyes, skin, and respiratory tract in animals; at high concentrations, exposure causes narcosis. In rabbits, n-butyl alcohol causes moderate skin irritation upon contact and severe corneal irritation when instilled into the eyes [NIOSH 1991]. The dermal LD_{50} in rabbits ranges from 3,400 to 5,300 mg/kg [NIOSH 1991; IPCS 1987]. The oral LD_{50}s in rats ranges from 700 to 2,100 mg/kg [IPCS 1987]. The 4-hr LC_{50} for rats is 8,000 ppm [NIOSH 1991]. Death also occurred in two of six female rats that inhaled 9,000 ppm for 7 hr. Half of another group of female rats that inhaled 8,000 ppm for 7 hr also developed narcosis. However, females that inhaled 6,000 ppm were asymptomatic throughout and after the 7-hr exposure period [Nelson et al. 1989]. Mice exposed to 3,300 ppm for 7 hr showed no effects, and 6,600 ppm caused giddiness within 1 hr, prostration within 2 hr, and loss of reflexes after 3 hr, with respiratory failure, deep narcosis, and death in some animals [Clayton and Clayton 1981]. Guinea pigs exposed to 100 ppm for 4 hr/day, 6 days/week for a total of 64 exposures showed lymphocytopenia and erythropenia; at autopsy, lung hemorrhage and degeneration of the liver and kidneys were seen [Clayton and Clayton 1981]. Groups of female rats were exposed to 8,000, 6,000, 3,500, or 0 ppm sec-butyl alcohol for 7 hr/day on gestation days 1 through 19. Absorbed daily doses for each of these exposure concentrations were *theorized to be 800, 600, 350, or 0* mg/kg, respectively. Two of 18 dams exposed at 8,000 ppm died. Fetal weights were slightly depressed at 8,000 and 6,000 ppm. A slight but statistically significant increase in skeletal malformations (primarily rudimentary cervical ribs) occurred in pups obtained from 8,000-ppm-exposed dams who exhibited the presence of maternal toxicity (reduced weight gain and food consumption) [Nelson et al. 1989]. n-Butyl alcohol was not mutagenic when tested with in vitro assays [IPCS 1987]. Two long-term n-butyl alcohol tests have been performed but were considered inadequate for assessment of carcinogenic activity [IPCS 1987].

2. *Effects on Humans*: n-Butyl alcohol causes eye, skin, and upper respiratory tract irritation in exposed workers. Volunteers reported mild irritation of the eyes, nose, and throat when exposed to 25 ppm. Unacclimatized subjects exposed to 50 ppm experienced pronounced throat irritation, and several of them developed delayed onset headaches [ACGIH 1991a]. Workers chronically exposed to 100 ppm rarely complained of eye irritation, where as previous exposures to 200 ppm or more caused corneal inflammation, an ocular burning sensation, blurred vision, lacrimation, and photophobia [ACGIH 1991a]. Repeated or prolonged contact of n-butyl alcohol with the skin causes defatting and contact dermatitis, and this substance can be absorbed through the skin in toxic amounts [Proctor et al. 1988].

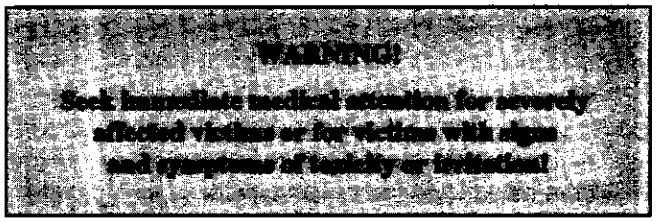
Vertigo and auditory nerve and vestibular system damage have been reported in Mexican and French workers exposed both to n-butyl alcohol and workplace noise, but the relative contribution of the alcohol to these effects has not been determined [ACGIH 1991a; Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to n-butyl alcohol can cause redness and tearing of the eyes, scratchy throat, itching and redness of the skin, headache, ataxia, prostration, deep narcosis, respiratory failure, and death.

2. *Chronic exposure*: Chronic exposure to n-butyl alcohol can cause photophobia, blurred vision, corneal vacuoles, and defatting and itching of the skin. Chronic exposure to n-butyl alcohol can cause vertigo and may increase the extent of hearing loss among workers exposed to both noise and n-butyl alcohol.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of n-butyl alcohol. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of n-butyl alcohol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if n-butyl alcohol or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve n-butyl alcohol and may result in worker exposures to this substance:

—Formulation of nitrocellulose lacquers, latexes, rayon detergents, esters, other butyl compounds, and plastic and rubber cements

—Use of n-butyl alcohol as a solvent or diluent in brake fluids, perfumes, detergents, adhesives, denatured alcohol, surface coatings, fats, waxes, natural and synthetic paints, resins, shellac, varnishes, gums, vegetable oils, dyes, camphor, and alkaloids

—Manufacture of artificial leather, safety glass, derivatives of butyl alcohol (including chemicals, herbicides, flotation agents, and urea and melamine formaldehyde resins), pharmaceuticals (including antibiotics, hormones, and vitamins), and bactericides for veterinary use

—Use of n-butyl alcohol during photographic processing operations and in the manufacture of photographic film

—Use of n-butyl alcohol in textile making as a swelling agent, dye ingredient, and waterproofing agent

—Use of n-butyl alcohol as an azeotropic dehydration agent and blending agent in laboratory analysis and in microscopy to prepare paraffin imbedding materials

The following methods are effective in controlling worker exposures to n-butyl alcohol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to n-butyl alcohol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to n-butyl alcohol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to n-butyl alcohol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of n-butyl alcohol on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-butyl alcohol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-butyl alcohol is determined by using charcoal tubes (100/50-mg sections, 20/40 mesh). To determine TWA concentrations, samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected; to determine ceiling limit concentrations, samples are collected for a minimum of

5 min. The sample is desorbed with carbon disulfide/isopropanol (99:1) or carbon disulfide/dimethylformamide (99:1). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method No. 1401 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If n-butyl alcohol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with n-butyl alcohol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of n-butyl alcohol, particularly its potential to be absorbed through the skin.

A worker who handles n-butyl alcohol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where n-butyl alcohol or a solution containing n-butyl alcohol is handled, processed, or stored.

STORAGE

n-Butyl alcohol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical service in the storage area must meet OSHA requirements for Class IC flammable liquids [29 CFR 1910.106]. Small amounts of n-butyl alcohol should be stored in metal safety cans in OSHA-approved safety cabinets or storerooms. Containers of n-butyl alcohol should be protected from physical damage and should be stored separately from oxidizing agents, strong mineral acids, alkali metals, halogens, explosives, organic peroxides, radioactive materials, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle n-butyl alcohol. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained n-butyl alcohol may hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving n-butyl alcohol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the n-butyl alcohol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Butyl alcohol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for n-butyl alcohol is 5,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of n-butyl alcohol per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-butyl alcohol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. n-Butyl alcohol is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. U031. This chemical is approved for land disposal as long as the concentration in the waste or treatment residual does not exceed 2.6 mg/kg. n-Butyl alcohol also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-butyl alcohol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. If the use of respirators is necessary, the only respirators permitted are those approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with n-butyl alcohol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon® has been recommended for use against permeation by n-butyl alcohol and may provide protection for periods greater than 8 hr. Materials that may withstand permeation for more than 4 but fewer than 8 hr are butyl rubber, neoprene, nitrile rubber, polyethylene, and polyethylene/ethylene vinyl alcohol. Polyvinyl alcohol and polyvinyl chloride provide questionable protection from permeation, and natural rubber has demonstrated poor resistance to permeation by n-butyl alcohol.

If n-butyl alcohol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which n-butyl alcohol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-butyl alcohol. Contact lenses should not be worn if the potential exists for n-butyl alcohol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR sec-BUTYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about sec-butyl alcohol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{10}O$

- **Structure**

$CH_3CH_2CH(OH)CH_3$

- **Synonyms**

2-Butanol, sec-butanol, 2-butyl alcohol, methyl ethyl carbinol, butylene hydrate, 2-hydroxybutane

- **Identifiers**

1. CAS No.: 78-92-2
2. RTECS No.: EO1750000
3. DOT UN: 1120 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

sec-Butyl alcohol is a colorless, flammable, volatile liquid with a strong, winelike odor. The odor threshold is reported to be between 0.4 and 2.5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (760 mm Hg): 99.5°C (211.1°F)
3. Specific gravity (water = 1): 0.81 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of sec-butyl alcohol): 2.55
5. Melting point: −115°C (−175°F)
6. Vapor pressure at 20°C (68°F): 12 mm Hg
7. Solubility: Moderately soluble in water; miscible with alcohol, ether, and most organic solvents
8. Evaporation rate (butyl acetate = 1): 1.3

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. sec-Butyl alcohol auto-oxidizes to form an explosive peroxide.
2. Incompatibilities: Fires and explosions may result from contact of sec-butyl alcohol with strong oxidizers, organic peroxides, or perchloric or permonosulfuric acid. sec-Butyl alcohol ignites on contact with chromium trioxide.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released when sec-butyl alcohol decomposes.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (dangerous fire hazard) to sec-butyl alcohol.

1. Flash point: 24°C (75°F)
2. Autoignition temperature: 405°C (761°F)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Flammable limits in air at 100°C (212°F) (% by volume): Lower, 1.7; upper, 9.8

4. Extinguishant: Use alcohol foam, carbon dioxide, or dry chemical to fight fires involving sec-butyl alcohol. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving sec-butyl alcohol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Vapors may travel to a source of ignition and flash back. Vapor explosion hazards may occur indoors, outdoors, or in sewers. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of sec-butyl alcohol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving sec-butyl alcohol. Firefighters' protective clothing may not provide protection against permeation by sec-butyl alcohol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for sec-butyl alcohol is 100 ppm (305 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 100 ppm (305 mg/m^3) as an 8-hr TWA and 150 ppm (455 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned sec-butyl alcohol a threshold limit value (TLV) of 100 ppm (303 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risks of narcosis and irritation associated with exposure to sec-butyl alcohol.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to sec-butyl alcohol can occur through inhalation, ingestion, and eye or skin contact.

• *Summary of toxicology*

1. *Effects on Animals*: In animals, sec-butyl alcohol is an eye irritant and, at high concentrations, a narcotic. Although it is not an irritant when in contact with rabbit skin, it can induce severe corneal injury when directly instilled into the eyes of rabbits [Grant 1986; NLM 1991]. Five of six rats died following an exposure of 16,000 ppm for 4 hr [Clayton and Clayton 1981]. Death also occurred in all five female rats that inhaled 10,000 ppm for 7 hr. Another group of female rats exposed to 7,000 ppm for 7 hr did not die and had not completely recovered from the induced narcosis on the day following exposure. Female rats exposed to 5,000 ppm also had impaired motor activity and developed narcosis [Nelson et al. 1989]. Inhalation of 10,670 ppm for 225 min or 16,000 ppm for 160 min was fatal to exposed mice [Clayton and Clayton 1981]. Mice that inhaled exposures ranging from 3,300 ppm for 5 hr to 19,800 ppm for 40 min developed restlessness, ataxia, prostration, and narcosis but did not die [NLM 1991]. Mice were unaffected by exposure to 1,650 ppm for 7 hr [ACGIH 1991a]. The oral LD_{50} in the rat is 6.5 g/kg [NIOSH 1991]. Mice exposed repeatedly to a sec-butyl alcohol concentration of 5,330 ppm for a total of 117 hr developed narcosis but survived the exposure [Clayton and Clayton 1981]. Groups of female rats were exposed to 7,000, 5,000, 3,500, or 0 ppm sec-butyl alcohol for 7 hr/day on gestation days 1 through 19. Absorbed daily doses for each of these respective exposure concentrations were theorized to be 700, 500, 350, or 0 mg/kg. No deaths occurred, but weight gain and food consumption were depressed for dams at each sec-butyl alcohol exposure concentration. The number of live fetuses was significantly reduced, resorptions increased, and the fetal weights were slightly depressed at 7,000 and 5,000 ppm [Nelson et al. 1989]. In two mutagenicity assays, *Schizosaccharomyces pombe* (yeast) and V-79 Chinese hamster cells, sec-butyl alcohol was nonmutagenic [IPCS 1987].

2. *Effects on Humans*: sec-Butyl alcohol has a defatting effect on the skin [Proctor et al. 1988]. Workers repeatedly exposed to 100 ppm have not developed signs or symptoms

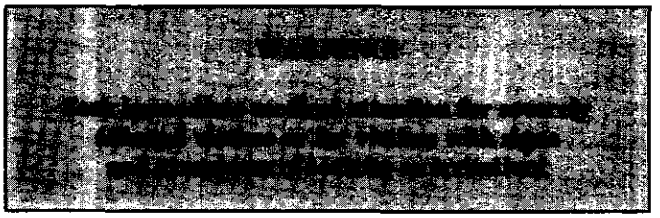
of toxicity or irritation [Proctor et al. 1988]. However, two patients who had become sensitized to primary alcohols tested positive when challenged with sec-butyl alcohol [NLM 1991]. Excessive exposure may result in headache, dizziness, drowsiness, and narcosis [IPCS 1987].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to sec-butyl alcohol can cause eye, nose, and throat irritation, with redness and tearing of the eyes, runny nose, defatting of skin, and cough. Exposure to high concentrations of sec-butyl alcohol is likely to cause headache, fatigue, nausea, dizziness, and narcosis.

2. *Chronic exposure*: Chronic exposure to sec-butyl alcohol can cause dermatitis in chronically exposed workers and may cause intense dermal sensitization in some exposed individuals.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of sec-butyl alcohol. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of sec-butyl alcohol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if sec-butyl alcohol or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve sec-butyl alcohol and may result in worker exposures to this substance:

—Use of sec-butyl alcohol as an adhesive in the manufacture of plywood and as a chemical intermediate in the production of methyl ethyl ketone, sec-butyl acetate, and xanthate

—Use of sec-butyl alcohol as a solvent for natural resins, linseed oil, castor oil, lacquer, paint removers, and adhesives

—Manufacture of flotation agents, hydraulic fluids, flavors, perfumes, dyestuffs, wetting agents, paint removers, industrial cleaners, and polishes

—Use of sec-butyl alcohol as a dehydrating agent, an antifoaming agent, and an ingredient in dewaxing paraffin

The following methods are effective in controlling worker exposures to sec-butyl alcohol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. *Industrial ventilation—a manual of* recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to sec-butyl alcohol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to sec-butyl alcohol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, and respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to sec-butyl alcohol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of sec-butyl alcohol on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for sec-butyl alcohol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne sec-butyl alcohol is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The samples are desorbed either with carbon disulfide/isopropanol (99:1) or carbon disulfide/dimethylformamide (99:1). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg/sample. This method is described in Method No. 1401 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If sec-butyl alcohol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with sec-butyl alcohol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of sec-butyl alcohol, particularly its potential to be irritating to the eyes and skin.

A worker who handles sec-butyl alcohol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where sec-butyl alcohol is handled, processed, or stored.

STORAGE

sec-Butyl alcohol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet OSHA requirements for Class IC flammable liquids. Drums must be equipped with self-closing valves, pressure-vacuum bungs, and flame arrestors. Containers of sec-butyl alcohol should be protected from physical damage and should be kept separate from oxidizing agents, explosives, heat, sparks, and open flame. Small amounts of this substance may be stored in metal safety cans in OSHA-approved safety cabinets or storage rooms. Only nonsparking tools may be used to handle sec-butyl alcohol. To prevent static sparks, containers should be grounded and bonded during transfers. Because containers that formerly contained sec-butyl alcohol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving sec-butyl alcohol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the sec-butyl alcohol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

sec-Butyl alcohol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of sec-butyl alcohol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of sec-butyl alcohol per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of sec-butyl alcohol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although sec-butyl alcohol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local

authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of sec-butyl alcohol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with sec-butyl alcohol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by sec-butyl alcohol and may withstand permeation for more than 4 but fewer than 8 hr: butyl rubber and polyethylene/ethylene vinyl alcohol.

If sec-butyl alcohol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which sec-butyl alcohol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with sec-butyl alcohol. Contact lenses should not be worn if the potential exists for sec-butyl alcohol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR tert-BUTYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about tert-butyl alcohol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{10}O$

- **Structure**

$(CH_3)_3COH$

- **Synonyms**

tert-Butanol; 2-methyl-2-propanol; TBA; t-butyl hydroxide; 1,1-dimethylethanol; trimethylmethanol; trimethylcarbinol

- **Identifiers**

1. CAS No.: 75-65-0
2. RTECS No.: EO1925000
3. DOT UN: 1120 26
4. DOT label: Flammable Liquid

- **Appearance and odor**

tert-Butyl alcohol is a colorless, crystalline solid or a volatile liquid (above 77°F) that has a camphorlike odor. The odor threshold is reported to be below 0.8 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (760 mm Hg): 82.4°C (180°F)
3. Specific gravity (water = 1): 0.79 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of tert-butyl alcohol): 2.55
5. Melting point: 25.6°C (78.1°F)
6. Vapor pressure at 20°C (68°F): 31 mm Hg
7. Solubility: Soluble in water; miscible with alcohol and ether
8. Evaporation rate (butyl acetate = 1): 1.05

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact with oxidizing agents, strong mineral acids, or strong hydrochloric acid.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide or isobutylene) may be released when tert-butyl alcohol decomposes in contact with strong mineral acids.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (dangerous fire hazard) to tert-butyl alcohol.

1. Flash point: 11°C (52°F) (closed cup)
2. Autoignition temperature: 478°C (892°F)

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3. Flammable limits in air (% by volume): Lower, 2.4; upper, 8.0

4. Extinguishant: Use dry chemical, carbon dioxide, alcohol foam, or water fog to fight fires involving tert-butyl alcohol. Blanket the fire to smother it. Water may be ineffective in extinguishing the fire, but a water spray may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to dilute spills to a nonflammable mixture.

Fires involving tert-butyl alcohol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapors may travel to a source of ignition and then flash back. Vapor explosions may occur indoors, outdoors, or in sewers. Containers of tert-butyl alcohol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving tert-butyl alcohol. Firefighters' protective clothing may not provide protection against permeation by tert-butyl alcohol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for tert-butyl alcohol is 100 ppm (300 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 150 ppm (450 mg/m^3) as a 15-min short-term exposure limit (STEL). A STEL is a 15-min TWA concentration that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 100 ppm (300 mg/m^3) as an 8-hr TWA and 150 ppm (450 mg/m^3) as a STEL [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned tert-butyl alcohol a threshold limit value (TLV) of 100 ppm (303 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek with a STEL of 150 ppm (455 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of narcotic effects associated with exposure to tert-butyl alcohol.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to tert-butyl alcohol can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: tert-Butyl alcohol causes narcosis in animals exposed to high concentrations. The oral LD_{50} in rats is 3,500 mg/kg [NIOSH 1991]. Prolonged contact of tert-butyl alcohol with the skin of rabbits caused no irritation [Clayton and Clayton 1981]. When six female rats were exposed to 10,000 ppm for 7 hr, all developed severe narcosis and five died. Female rats in another group that inhaled 5,000 ppm for 7 hr also developed ataxia and narcosis but did not die. A 2,000-ppm exposure resulted in ataxia alone [Nelson et al. 1989]. Compared with other butyl alcohols, tert-butyl alcohol is reported to have a stronger narcotic effect on mice and rats [ACGIH 1991a; Nelson et al. 1989]. Rats given nontoxic oral doses of tert-butyl alcohol (0.0163 mol/kg) showed a marked decline in motor performance test scores; tert-butyl alcohol caused a narcotic effect estimated to be 4.8 times greater than that of ethanol [Clayton and Clayton 1981]. In a teratology study, groups of pregnant rats were exposed to 5,000, 3,500, 2,000, or 0 ppm tert-butyl alcohol for 7 hr/day during gestation days 1 through 19. Absorbed daily doses for each of these respective exposure levels were theorized to be 500, 350, 200, or 0 mg/kg. Depressed maternal weight gain and food consumption were induced only at 5,000 ppm. Fetal weights were statistically depressed in a dose-related fashion for all three alcohol exposures, and skeletal variations were statistically increased only at 5,000 and 3,500 ppm [Nelson et al. 1989]. The effect of prenatal ethanol or tert-butyl alcohol exposure on postnatal development was studied in mice. Daily ingestion of a diet deriving 1% of its calories from tert-butyl alcohol reduced maternal weight gain and food consumption and increased the number of stillborn pups. The authors concluded that this compound was five times more potent than ethanol in producing developmental delay in postnatal physiologic and psychomotor performance [Daniel and Evans 1982]. Ethanol and tert-butyl alcohol exposures were also compared for their potential to induce microcephaly in neonatal rats. Using an artificial rearing technique and exposures during developmental

days 4 through 7, microcephaly was induced by both of these alcohols [Grant and Sampson 1982]. This compound has been tested in a wide variety of mutagenicity assays, all of which confirm it to be a nonmutagen [IPCS 1987]. The National Toxicology Program (NTP) has completed one carcinogenicity study in mice and rats administered tert-butyl alcohol in drinking water. However, they judged this study to be inadequate for publication. The NTP has also completed subchronic tert-butyl alcohol inhalation studies in mice and rats and intends to conduct a set of inhalation carcinogenicity studies in these species [NTP 1992].

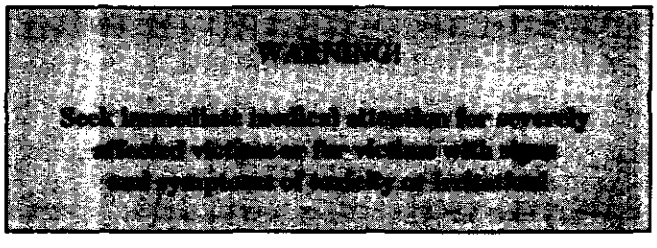
2. *Effects on Humans*: tert-Butyl alcohol causes eye and mucous membrane irritation. In contact with the skin of humans, tert-butyl alcohol caused slight redness, hyperemia, and irritation; prolonged skin contact may cause contact dermatitis [Clayton and Clayton 1981; NLM 1991]. A positive patch test was found in an individual who had an allergic skin reaction to a skin screen that contained tert-butyl alcohol [ACGIH 1991a]. Exposure to excessive (not further specified) concentrations caused eye, nose, and throat irritation, headache, nausea, fatigue, dizziness, and narcosis in humans [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to tert-butyl alcohol can cause irritation and redness of the eyes, runny nose, scratchy throat, headache, nausea, fatigue, dizziness, and redness and drying of the skin.

2. *Chronic exposure*: Chronic exposure to tert-butyl alcohol can cause defatting of the skin and dermatitis.

- **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of tert-butyl alcohol. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of tert-butyl alcohol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if tert-butyl alcohol or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve tert-butyl alcohol and may result in worker exposures to this substance:

—Use of tert-butyl alcohol as a solvent for paints, lacquers, varnishes, natural and synthetic resins, gums, vegetable oils, dyes, camphor, and alkaloids, and as an octane booster in unleaded gasoline

—Manufacture of artificial leather, safety glass, rubber and plastic cements, shellac, raincoats, photographic films, flotation agents, fruit essences, perfumes, cellulose esters, lacquers, paint removers, and plastics

—Use of tert-butyl alcohol as a denaturant for alcohol and as a chemical intermediate in the manufacture of methyl methacrylate and pharmaceuticals

The following methods are effective in controlling worker exposures to tert-butyl alcohol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to tert-butyl alcohol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to tert-butyl alcohol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to tert-butyl alcohol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of tert-butyl alcohol on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for tert-butyl alcohol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne tert-butyl alcohol is determined by using charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected (for TWA monitoring) or a maximum air volume

of 3 liters is collected (for STEL monitoring). The sample is then desorbed with carbon disulfide/2-butanol (99:1) or with carbon disulfide/dimethylformamide (99:1) to extract the tert-butyl alcohol. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg per sample. This method is described in the OSHA Computerized Information System [OSHA 1990] and in Method 1400 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If tert-butyl alcohol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing and shoes contaminated with tert-butyl alcohol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of tert-butyl alcohol, particularly its potential for irritating the skin.

A worker who handles tert-butyl alcohol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where tert-butyl alcohol is handled, processed, or stored.

STORAGE

tert-Butyl alcohol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of tert-butyl alcohol should be protected from physical damage and should be stored separately from strong oxidizers, strong mineral acids, strong hydrochloric acid, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure-vacuum bungs, and flame arrestors. Only nonsparking tools and equipment may be used to handle tert-butyl alcohol. To prevent static sparks, containers of tert-butyl alcohol should be grounded and bonded for transfers. Because containers that formerly contained tert-butyl alcohol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving tert-butyl alcohol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors, but be aware that the spray may not prevent ignition in closed spaces.
6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the tert-butyl alcohol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

tert-Butyl alcohol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of tert-butyl alcohol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of tert-butyl alcohol per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of tert-butyl alcohol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although tert-butyl alcohol is not specifically listed as a hazardous waste under the Resource Conservation and

Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of tert-butyl alcohol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with tert-butyl alcohol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Butyl rubber has been tested against permeation by tert-butyl alcohol and has demonstrated good-to-excellent resistance for periods greater than 8 hr. Polyethylene ethylene/vinyl alcohol may withstand permeation for more than 4 but fewer than 8 hr.

If tert-butyl alcohol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which tert-butyl alcohol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with tert-butyl alcohol. Contact lenses should not be worn if the potential exists for tert-butyl alcohol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BUTYLAMINE

INTRODUCTION

This guideline summarizes pertinent information about butylamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_4H_{11}N$

- **Structure**

$CH_3CH_2CH_2CH_2NH_2$

- **Synonyms**

1-Butylamine, n-butylamine, 1-aminobutane, 1-butanamine, Norvalamine, mono-n-butylamine

- **Identifiers**

1. CAS No: 109-73-9
2. RTECS No.: EO2975000
3. DOT UN: 1125 68
4. DOT label: Flammable Liquid

- **Appearance and odor**

Butylamine is a colorless, volatile, flammable liquid with an ammonialike odor; the liquid tends to yellow on standing. The odor threshold is reported to be 1.8 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 73.1
2. Boiling point (760 mm Hg): 78°C (172°F)
3. Specific gravity (water = 1): 0.74 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of butylamine): 2.5
5. Melting point: -50°C (-58°F)
6. Vapor pressure at 20°C (68°F): 82 mm Hg
7. Solubility: Miscible with water, alcohol, and ether
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosion may result from contact of butylamine with strong oxidizers or strong acids.
3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving butylamine.
4. Special precautions: In the presence of moisture, butylamine corrodes some metals on contact.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (dangerous fire hazard) to butylamine.

1. Flash point: -12°C (10°F) (closed cup)
2. Autoignition temperature: 312°C (594°F)
3. Flammable limits in air (% by volume): Lower, 1.7; upper, 9.8
4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving butylamine. Water may be an ineffective extinguishant, but it may be used to cool

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fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving butylamine should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of butylamine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving butylamine. Firefighters' protective clothing may not provide protection against permeation by butylamine.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for butylamine is 5 ppm (15 mg/m^3) as a ceiling limit. A worker's exposure to butylamine shall at no time exceed this ceiling limit. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (15 mg/m^3) as a ceiling limit with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned butylamine a ceiling limit of 5 ppm (15 mg/m^3), which should not be exceeded during any part of the working exposure. The ACGIH also assigns a "Skin" notation to butylamine [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye, skin, and respiratory tract irritation associated with exposure to butylamine.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to butylamine can occur through inhalation, ingestion, eye or skin contact, and by skin absorption.

• Summary of toxicology

1. *Effects on Animals*: Butylamine vapor is an irritant of the eyes, nose, respiratory tract, and skin; contact of liquid butylamine with the eyes or skin causes corrosive burns. The oral LD_{50} in rats is 366 mg/kg, the LC_{50} in rats is 4,000 ppm for 4 hr, and the dermal LD_{50} in rabbits is 850 mg/kg [NIOSH 1991]. Rats exposed for an unspecified time to butylamine at concentrations of 3,000 to 5,000 ppm exhibited signs of severe irritation of the respiratory tract, developed pulmonary edema, and died within minutes or hours of the exposure [Clayton and Clayton 1981]. When applied to the skin of guinea pigs, butylamine caused necrosis [ACGIH 1991a]. Butylamine caused severe damage to the eyes of rabbits [ACGIH 1991a].

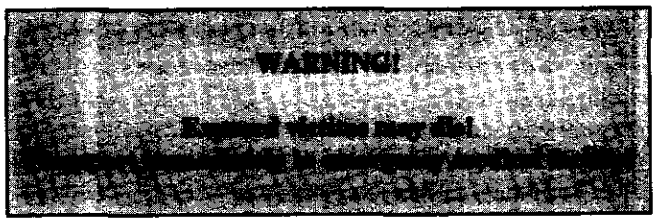
2. *Effects on Humans*: Exposure to butylamine vapor causes eye, nose, and upper respiratory tract irritation, and contact of the skin or eyes with liquid butylamine causes severe irritation, corrosive burns, and possibly blindness [Clayton and Clayton 1981]. Workers exposed to butylamine concentrations at 5 to 10 ppm or higher experience eye and upper respiratory tract irritation, and exposure to butylamine concentrations at 10 to 25 ppm for more than a few minutes is considered intolerable by some workers [Clayton and Clayton 1981; Proctor et al. 1988].

• Signs and symptoms of exposure

1. *Acute exposure*: The signs and symptoms of acute exposure to butylamine include redness and tearing of the eyes, runny nose, scratchy throat, headache, facial flushing, increased pulse and respiratory rates, shortness of breath, and (if the exposure is severe) hyperactive reflexes, cyanosis, pulmonary edema, convulsions, and coma. If absorbed through the skin in toxic amounts, butylamine can cause nausea, vomiting, and shock. Direct eye or skin contact with the liquid can result in deep second-degree burns, blistering, corrosion, and possible blindness. Oral administration of near-lethal doses of butylamine to rats and rabbits resulted in hyperactivity of the reflexes, an increase in pulse and respiratory rates, shortness of breath, convulsions, cyanosis, and coma [ACGIH 1991a]. Some workers exposed to this substance at 5 to 10 ppm also experienced headache and facial flushing [Proctor et al. 1988].

2. *Chronic exposure*: No signs or symptoms of chronic exposure to butylamine have been reported.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of butylamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of butylamine are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if butylamine or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve butylamine and may result in worker exposures to this substance:

—Use of butylamine as a vulcanizing accelerator and reaction initiator in the rubber and polymer industries

—Use of butylamine as a chemical intermediate in the production of emulsifying agents, rubber chemicals, synthetic tanning agents, and special soaps

—Manufacture of photographic developers, pharmaceuticals, dyes, gasoline antioxidants, insecticides, and textile desizing agents

—Use of butylamine as a flavoring ingredient in alcoholic beverages, ice cream, ices, candy, baked goods, gelatins, and puddings

The following methods are effective in controlling worker exposures to butylamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to butylamine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to butylamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to butylamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of butylamine on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. However, no biological monitoring test acceptable for routine use has yet been developed for butylamine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne butylamine is determined by using sulfuric-acid-coated silica gel tubes (150/75-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 15 liters is collected. The samples are desorbed with methanol/water (50:50). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is not known. This method is described in Method No. S138 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

Butylamine causes severe burns on contact with the skin; this substance can also be absorbed through the skin in toxic amounts. Therefore, if butylamine contacts the skin, workers should flush the affected areas immediately with plenty of water for at least 15 min and then wash with soap and water. Get medical attention immediately.

Clothing and shoes contaminated with butylamine should be removed immediately, and provisions should be made for

safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of butylamine, particularly its potential to be absorbed through the skin and to cause eye and skin burns.

A worker who handles butylamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where butylamine or a solution containing butylamine is handled, processed, or stored.

STORAGE

Butylamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard storage area or room for flammable liquids. All ventilation systems and electrical equipment in storage areas should be of explosionproof design. Containers of butylamine should be protected from physical damage and should be stored separately from strong oxidizers and strong acids, heat, sparks, and open flame. To prevent static sparks, all containers and equipment used in shipping, transferring, or receiving operations should be bonded and grounded. Because containers that formerly contained butylamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving butylamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to cool fire-exposed containers and to reduce vapors; such spraying may not prevent ignition in closed spaces.
6. Absorb small spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large spills, build dikes far ahead of the spill to contain the butylamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Butylamine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for butylamine is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of butylamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reac-

tivity, or toxicity as defined in 40 CFR 261.21-261.24. Although butylamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of butylamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any possibility of skin contact with butylamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Teflon® has been recommended for use against permeation by butylamine and may withstand permeation for more than 4 but fewer than 8 hr. Butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl alcohol, polyvinyl chloride, and Viton® have demonstrated poor resistance to permeation by butylamine.

If butylamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which butylamine might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with butylamine. Contact lenses should not be worn if the potential exists for butylamine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR tert-BUTYL CHROMATE

INTRODUCTION

This guideline summarizes pertinent information about tert-butyl chromate (measured as chromate) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_8H_{18}CrO_4$

- **Structure**

  $[(CH_3)_3CO]_2CrO_2$

- **Synonyms**

  t-Butyl chromate; bis(tert-butyl)chromate; chromic acid, di-tert-butyl ester.

- **Identifiers**

  1. CAS No.: 1189-85-1
  2. RTECS No.: GB2900000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  tert-Butyl chromate is a clear, colorless liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 230.3
  2. Boiling point: Data not available
  3. Specific gravity: Data not available
  4. Vapor density (air = 1 at boiling point of tert-butyl chromate): 7.9
  5. Melting point: -5° to 0°C (23° to 32°F)
  6. Vapor pressure: Data not available
  7. Solubility: tert-Butyl chromate is miscible with water
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame may ignite the flammable liquid solution used as a carrier for shipping tert-butyl chromate.

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2. Incompatibilities: Contact of tert-butyl chromate with reducing agents and moisture should be avoided, and contact with acids, alcohols, and combustible organic or easily oxidized materials (such as paper, wood, plastic, aluminum, and sulfur) may cause a violent reaction.

3. Hazardous decomposition products: Acrid and irritating fumes and poisonous gases may be released in a fire involving tert-butyl chromate.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to tert-butyl chromate. Other sources rate tert-butyl chromate as a dangerous fire hazard.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, sand, water spray, or foam to extinguish fires involving tert-butyl chromate.

Fires involving tert-butyl chromate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of tert-butyl chromate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if a rising sound from a venting safety device is heard or if there is discoloration of a container due to fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving tert-butyl chromate. Structural fire-fighters' protective clothing will provide limited protection against fires involving tert-butyl chromate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for tert-butyl chromate (measured as chromate) is 0.1 mg/m^3 as a ceiling limit. A worker's exposure to tert-butyl chromate shall at no time exceed this ceiling level. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers tert-butyl chromate a potential human carcinogen and has issued a recommended exposure limit (REL) for tert-butyl chromate (measured as hexavalent chromium) of 1 g/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned tert-butyl chromate (measured as chromate) a ceiling limit value of 0.1 mg/m^3, which should not be exceeded during any part of the working exposure. The ACGIH also assigns a "Skin" notation to tert-butyl chromate [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the inferred risk of cancer associated with exposure to this substance [NIOSH 1992]. The ACGIH limit is based on the risk of pulmonary changes, narcosis, and necrotic lesions of the skin associated with exposure to this substance [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to tert-butyl chromate can occur through

inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* tert-Butyl chromate is a hexavalent chromium compound. Although there are no acute toxicity data specifically for this chromate, hexavalent chromium compounds are known to cause cancer in experimental animals, including lung cancers, injection-site tumors, and cancer of the kidneys [Langard 1988]. In contact with the skin of animals, tert-butyl chromate causes necrosis of the skin at the site of contact; death caused by percutaneous absorption of lethal quantities of this substance also occurs [ACGIH 1991]. Rats exposed repeatedly for 30 to 60 minutes/day to an unspecified but lethal concentration of tert-butyl chromate and butyl alcohol showed signs of respiratory and skin irritation and behavioral changes before death [ACGIH 1991]. At autopsy, lung edema and fatty deposition in the liver were seen in these animals [ACGIH 1991]. In another study, exposure of rats to tert-butyl chromate alone (concentration not specified) caused an increase in respiratory rate and signs of mild narcosis [ACGIH 1991].

2. *Effects on Humans:* NIOSH classifies all hexavalent chromium compounds, including tert-butyl chromate, as potential occupational carcinogens. However, there is little toxicity information specifically for organic hexavalent compounds, including tert-butyl chromate. In humans, tert-butyl chromate causes acid-like burns and necrotic lesions in contact with the eyes or skin, and exposure to the vapor of this substance causes irritation of the upper respiratory tract and may lead to ulceration of the nasal septum [NJDH 1987]. Skin contact can also cause an allergic rash in sensitive individuals, and long-term exposure may lead to kidney or liver damage [NJDH 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to tert-butyl chromate include redness and inflammation of the eyes and eyelids, runny nose, sore throat, coughing, nose bleeds, nasal discharge, crusting or sores in the nose, and skin and eye burns.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to tert-butyl chromate include perforation of the nasal septum, jaundice, enlarged and tender liver, and blood, pus, or protein in the urine.

- **Emergency procedures**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of tert-butyl chromate! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if tert-butyl chromate or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cav-

ity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve tert-butyl chromate and lead to worker exposures to this substance:

—Use in specialty reactions as an organic source of chromium

—Manufacture of catalysts

—Use for polymerizing olefins and as a curing agent for urethane resins

The following methods are effective in controlling worker exposures to tert-butyl chromate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to tert-butyl chromate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concen-

trate on the function and integrity of the eyes, skin, respiratory tract, kidneys, and liver. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to tert-butyl chromate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin or respiratory allergies or findings consistent with diseases of the eyes, skin, respiratory tract, kidneys, or liver.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to tert-butyl chromate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of tert-butyl chromate on the eyes, skin, respiratory tract, kidney, or liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urinary chromium concentrations correlate well with airborne chromium concentrations and are believed to be good indicators of recent short-term exposure. A urinary chromium level of 40-50 g/liter urine, or 30 g per gram creatinine, is believed to correspond to exposure to an airborne chromium level of 0.05 mg/m3 [Baselt 1988].

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to tert-butyl chromate may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne tert-butyl chromate is made using a low ash polyvinyl chloride (LAPVC) 5-micron filter. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. The sample is then treated with a carbonate/bicarbonate buffer to extract the tert-butyl chromate. Analysis is conducted by polarographic analysis using differential pulse polarography. This method has a sampling and analytical error of 0.18 and is described in the OSHA Computerized Information System [OSHA 1993] and in Method ID-103 of the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

Because tert-butyl chromate can be absorbed through the skin in toxic amounts, workers should immediately wash any affected areas with soap and water.

Clothing contaminated with tert-butyl chromate should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of tert-butyl chromate, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles tert-butyl chromate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where tert-butyl chromate or a solution containing tert-butyl chromate is handled, processed, or stored.

STORAGE

tert-Butyl chromate should be stored in an explosion-proof refrigerator in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of tert-butyl chromate should be protected from physical damage and should be stored separately from reducing agents, moisture, acids, alcohols, and combustible organic or easily oxidized materials (such as paper, wood, plastic, aluminum, and sulfur), heat, sparks, and open flame. Because containers that formerly contained tert-butyl chromate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving tert-butyl chromate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Remove all sources of heat and ignition.

3. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

4. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

5. For large liquid spills, build dikes far ahead of the spill to contain the tert-butyl chromate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  tert-Butyl chromate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of tert-butyl chromate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and that manufacture 25,000 lb or more or otherwise use 10,000 lb or more of a chromium compound per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of such compounds emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although tert-butyl chromate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addi-

tion, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of tert-butyl chromate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with tert-butyl chromate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to tert-butyl chromate permeation; however, butyl rubber and polyvinyl chloride have been tested against a chemically similar material (chromic acid) and will potentially resist permeation for periods greater than 4 but fewer than 8 hours. Since specific test data are not available for tert-butyl chromate, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to tert-butyl chromate.

Safety glasses, goggles, or face shields should be worn during operations in which tert-butyl chromate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with tert-butyl chromate. Contact lenses should not be worn if the potential exists for tert-butyl chromate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL GLYCIDYL ETHER

INTRODUCTION

This guideline summarizes pertinent information about n-butyl glycidyl ether (BGE) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_7H_{14}O_2$
- **Structure:** $CH_3CH_2CH_2CH_2OCH_2CH(O)CH_2$

- **Synonyms:** BGE; butyl glycidyl ether; 2,3-epoxypropyl butyl ether; 1-butoxy-2,3-epoxypropane
- **Identifiers:** CAS 2426-08-6; RTECS TX4200000; DOT not assigned
- **Appearance and odor:** Colorless to pale yellow liquid with a slightly unpleasant odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.21
2. Boiling point (at 760 mmHg): 164°C (327°F)
3. Specific gravity (water = 1): 0.91
4. Vapor density (air = 1 at boiling point of BGE): 4.5
5. Vapor pressure at 20°C (68°F): 3 mmHg
6. Solubility in water, g/100 g water at 20°C (68°F): 2
7. Evaporation rate (butyl acetate = 1): 0.36
8. Saturation concentration in air (approximate) at 25°C (77°F): 0.42% (4,200 ppm)

- **Reactivity**

1. Incompatibilities: Contact between BGE and strong oxidizing agents may cause fires and explosions. Contact between BGE and strong caustics may cause polymerization with the liberation of heat, which may cause the container to burst. BGE should not be exposed to light or air because explosive peroxides may be formed.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving BGE.
3. Caution: BGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 54°C (130°F) (closed cup)
2. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
3. Class II Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, BGE should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for BGE is 50 parts of BGE per million parts of air (ppm) [270 milligrams of BGE per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 5.6 ppm (30 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 25 ppm (135 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for n-butyl glycidyl ether

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	50	270
NIOSH REL Ceiling (15 min)	5.6	30
ACGIH TLV® TWA	25	135

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• **Routes of exposure**

BGE may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**

Effects on animals: In rats and mice, acute inhalation or oral administration of BGE caused central nervous system depression, pulmonary edema, and death; intramuscular injection in rats produced increased white blood cell counts. Subchronic inhalation of BGE by rats produced testicular atrophy; dermal exposure of male mice that were subsequently bred to unexposed females produced an increased incidence of fetal deaths. BGE was mutagenic in bacterial test systems, and DNA damage was induced *in vitro* in human white blood cells.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to BGE can cause mild irritation of the skin, eyes, nose, and respiratory tract.
2. *Long-term (chronic):* Exposure to BGE can cause inflammation and sensitization of the skin.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to BGE, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and reproductive, nervous, respiratory, and hematopoietic (blood-cell-forming) systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to BGE at or below the NIOSH REL.

The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to BGE. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, and reproductive, nervous, respiratory, and hematopoietic systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

• **Sentinel health events**

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of BGE. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the peri-

ods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**
Sampling and analysis may be performed by collecting BGE vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure BGE may also be used if available. A detailed sampling and analytical method for BGE may be found in *NIOSH Manual of Analytical Methods* (method number S81).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with BGE.

Workers should be provided with and required to use splash-proof safety goggles where BGE may come in contact with the eyes.

SANITATION

Clothing which is contaminated with BGE should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of BGE from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of BGE's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with BGE should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle BGE should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to BGE may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for BGE

Operations	Controls
During use as a reactive diluent of epoxy resins	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a chemical intermediate for preparation of ethers, surfactants, polymers, and resins	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a stabilizing agent for organic chemicals	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**
Where there is any possibility of a worker's eyes being exposed to BGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If BGE gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**
Where there is any possibility of a worker's body being exposed to BGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If BGE gets on the skin, wash it immediately with soap and water. If BGE penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**
If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If BGE is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing BGE, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from BGE vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing BGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. BGE should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing BGE may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for n-butyl glycidyl ether

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 56 ppm	Any supplied-air respirator (substance reported to cause eye irritation or damage—may require eye protection)
	Any self-contained breathing apparatus (substance reported to cause eye irritation or damage—may require eye protection)
	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage may require eye protection)
Less than or equal to 140 ppm	Any supplied-air respirator operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 280 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 3,500 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 3,500 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 5.6 ppm (30 mg/m³) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL LACTATE

INTRODUCTION

This guideline summarizes pertinent information about n-butyl lactate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_7H_{14}O_3$

- **Structure**

$CH_3CH(OH)COOC_4H_9$

- **Synonyms**

Butyl α-hydroxypropionate; butyl lactate; 2-hydroxypropanoic acid, butyl ester; lactic acid, butyl ester

- **Identifiers**

1. CAS No.: 138-22-7
2. RTECS No.: OD4025000
3. DOT UN: 1993 27 (combustible liquid not otherwise specified)
4. DOT label: None

- **Appearance and odor**

n-Butyl lactate is a clear, colorless to white, combustible liquid. It has a mild, transient odor. The odor threshold is reported to be 7 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 146.2
2. Boiling point (760 mm Hg): 188°C (370.4°F)
3. Specific gravity (water = 1): 0.9 to 0.984 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of n-butyl lactate): 5.0
5. Melting point: -43°C (-45.4°F)
6. Vapor pressure at 20°C (68°F): 0.4 mm Hg
7. Solubility: Slightly soluble in water; miscible with alcohol and ether; hydrolyzed by acids and bases
8. Evaporation rate (butyl acetate = 1): 0.44

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame. Strong acids (such as hydrochloric, sulfuric, or nitric) and strong bases (such as sodium hydroxide) can cause butyl lactate to decompose.
2. Incompatibilities: A reaction may result from contact of n-butyl lactate with strong oxidizers.
3. Hazardous decomposition products: Toxic gases (such as carbon dioxide) may be released in a fire involving n-butyl lactate.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to n-butyl lactate.

1. Flash point: 71°C (160°F) (open cup)
2. Autoignition temperature: 382°C (720°F)
3. Flammable limits in air (% by volume): Lower, 1.15; upper, data not available
4. Extinguishant: Use water fog, dry chemical, alcohol foam, or carbon dioxide to fight fires involving n-butyl lactate. Do not use a solid stream of water because this will scatter and spread the fire. Water may be ineffective for fighting fires, but it may be used to cool fire-exposed containers.

Fires involving n-butyl lactate should be fought upwind and from the maximum distance possible. Isolate the hazard area

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and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of n-butyl lactate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving n-butyl lactate. Firefighters' protective clothing may not provide protection against permeation by n-butyl lactate.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butyl lactate is 5 ppm (25 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (25 mg/m^3) as an 8-hr TWA [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned n-butyl lactate a threshold limit value (TLV) of 5 ppm (30 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of headaches and irritation of pharyngeal and laryngeal mucosa associated with exposure to n-butyl lactate.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to n-butyl lactate can occur through inhalation, ingestion, or eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: n-Butyl lactate is an eye and respiratory tract irritant and a central nervous system depressant; it also causes a moderate degree of irritation to the skin of rabbits [NIOSH 1991]. The oral LD_{50} in rats is 5 g/kg [NIOSH 1991]. Acutely poisoned animals exhibit somnolence, flaccid paralysis, and dyspnea before death.

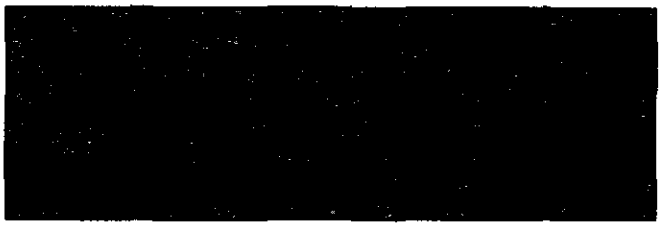
2. *Effects on Humans*: n-Butyl lactate is a central nervous system depressant and an irritant of the eyes, mucous membranes, and upper respiratory tract. Prolonged or repeated contact with the skin by n-butyl lactate causes defatting, redness, and cracking of the skin [Genium 1987]. Prolonged exposures to approximately 7 ppm with peak exposures to 11 ppm caused irritation of the pharyngeal and laryngeal mucosa, coughing, and complaints of sleepiness and headache in the evening after work [ACGIH 1991a]. Some workers also experienced nausea and vomiting [ACGIH 1991a]. Exposure to 4 ppm also caused some of these symptoms [ACGIH 1991a]. No symptoms were reported by workers exposed to n-butyl lactate at concentrations below 1.4 ppm [ACGIH 1991a].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to n-butyl lactate may cause coughing, scratchy throat, nausea, headache, dyspnea, vomiting, CNS depression, and redness, pain, and tearing of the eyes.

2. *Chronic exposure*: Prolonged or repeated contact with n-butyl lactate may cause ocular or mucosal irritation, dryness, redness, cracking, and defatting of the skin.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of n-butyl lactate. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of n-butyl lactate are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if n-butyl lactate or a solution containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses of n-butyl lactate may result in worker exposures to this substance:

—Use as a solvent for cellulose, varnishes, lacquers, stencil pastes, natural gums, oils, dyes, and many synthetic polymers

—Use in making paint, inks, perfumes, and dry cleaning fluids

—Use in making antiskinning agents and adhesives and as a chemical intermediate

The following methods are effective in controlling worker exposures to n-butyl lactate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to n-butyl lactate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific

job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to n-butyl lactate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to n-butyl lactate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of n-butyl lactate on the skin and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for n-butyl lactate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne n-butyl lactate is determined by using a charcoal tube (100/50-mg front and backup sections). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with a 95:5 mixture of methylene chloride and methanol to extract the n-butyl lactate. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1989] and in the OSHA Laboratory In-House Methods File [OSHA 1990].

PERSONAL HYGIENE

If n-butyl lactate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing and shoes contaminated with n-butyl lactate should be removed, and provisions should be made for safely removing this chemical from these articles.

A worker who handles n-butyl lactate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where n-butyl lactate or a solution containing n-butyl lactate is handled, processed, or stored.

STORAGE

n-Butyl lactate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet the requirements for OSHA Class IIIA [29 CFR 1910.106] combustible liquids. Containers of n-butyl lactate should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Only nonsparking tools may be used to handle n-butyl lactate. To prevent static sparks, containers and equipment must be grounded and bonded when transferring this material. Because containers that formerly contained n-butyl lactate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving n-butyl lactate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres using ventilation of explosionproof design.

5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

6. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the n-butyl lactate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

n-Butyl lactate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of n-butyl lactate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of n-butyl lactate emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although n-butyl lactate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of n-butyl lactate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged skin contact with n-butyl lactate. Impervious

gloves, aprons, boots, gauntlets, plastic coveralls, and other protective clothing should be worn as necessary when handling this material. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to n-butyl lactate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to n-butyl lactate.

If n-butyl lactate is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which n-butyl lactate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with n-butyl lactate. Contact lenses should not be worn if the potential exists for n-butyl lactate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR n-BUTYL MERCAPTAN

INTRODUCTION

This guideline summarizes pertinent information about n-butyl mercaptan for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_4H_{10}S$
- **Structure:** CH_3-$(CH_2)_2$-CH_2-SH
- **Synonyms:** n-Butanethiol; 1-butanethiol; butyl sulfhydrate; thiobutyl alcohol
- **Identifiers:** CAS 109-79-5; RTECS EK6300000; DOT 2347, label required: "Flammable Liquid"
- **Appearance and odor:** Clear, colorless liquid with a strong, obnoxious odor like garlic or skunk

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical Data**

1. Molecular weight: 90.19
2. Boiling point (at 760 mmHg): 97.8°C (208°F)
3. Specific gravity (water = 1): 0.8368
4. Vapor density (air = 1 at boiling point of n-butyl mercaptan): 3.1
5. Melting point: -116°C (-177°F)
6. Vapor pressure at 20°C (68°F): 35 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.06
8. Evaporation rate (butyl acetate = 1): 2.86
9. Saturation concentration in air (approximate) at 20°C (68°F): 4.6% (46,000 ppm)
10. Ionization potential: 9.14 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents; n-butyl mercaptan should not be stored in copper or copper-containing materials.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., sulfur dioxide and carbon monoxide) may be released in a fire involving n-butyl mercaptan.
3. Caution: n-Butyl mercaptan will attack some forms of plastics, coating, and rubber.

- **Flammability**

1. Flash point: 2°C (35°F)
2. Extinguishant: Carbon dioxide, dry chemicals, or foam
3. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 1.0 to 48 ppb
2. Evaluation of warning properties for respirator selection: Because of its odor, n-butyl mercaptan can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for n-butyl mercaptan is 10 parts of n-butyl mercaptan per million parts of air (ppm) [35 milligrams of n-butyl mercaptan per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 0.5 ppm (1.8 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (1.5 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for n-butyl mercaptan

	Exposure limit	
	ppm	mg/m³
OSHA PEL TWA	10	35
NIOSH REL ceiling (15 min)	0.5	1.8
ACGIH TLV® TWA	0.5	1.5

HEALTH HAZARD INFORMATION

- **Routes of exposure**

n-Butyl mercaptan may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

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• **Summary of toxicology**

1. *Effects on animals:* In mice and rats, inhalation of n-butyl mercaptan caused increased breathing rates, hyperactivity, uncoordinated movement, staggering gait, muscular weakness, partial skeletal muscle paralysis, deficient oxygenation of the blood (cyanosis), sedation, and death.

2. *Effects on humans:* In an industrial accident, seven workers were exposed to n-butyl mercaptan for approximately 1 hour at a concentration estimated between 50 and 500 ppm; all workers experienced some of the symptoms listed below, although the specific combination of symptoms varied for each individual.

• **Signs and symptoms of exposure**

Short-term (acute): Exposure to n-butyl mercaptan can cause irritation of the mucous membranes, weakness, malaise, increased respiration, neck pain, drowsiness, nausea, vomiting, sweating, dizziness, confusion, and coma.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to n-butyl mercaptan, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risk. These should concentrate on the function and integrity of the nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to n-butyl mercaptan at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic diseases of the respiratory system.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to n-butyl mercaptan. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of n-butyl mercaptan. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

Sampling and analysis may be performed by collecting n-butyl mercaptan vapors with Chromosorb 104 tubes, followed by desorption with acetone and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure n-butyl mercaptan may be used if available. A detailed sampling and analytical method for n-butyl mercaptan may be found in the *NIOSH Manual of Analytical Methods* (method number S350).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with n-butyl mercaptan.

Workers should be provided with and required to use splash-proof safety goggles where n-butyl mercaptan may come in contact with the eyes.

SANITATION

Clothing which is contaminated with n-butyl mercaptan should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of n-butyl mercaptan from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of n-butyl mercaptan's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with n-butyl mercaptan should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle n-butyl mercaptan should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to n-butyl mercaptan may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for n-butyl mercaptan

Operations	Controls
During the manufacture and processing of n-butyl mercaptan; during use as an odorant for natural gas	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a chemical intermediate in the manufacture of agricultural chemicals, herbicides, and defoliants	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the polymer industry in the manufacture of polymerization catalysts, stabilizers, modifiers, and chain transfer agents	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a solvent; during the cleaning and maintenance of storage vessels and equipment	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to n-butyl mercaptan, an eye-wash fountain should be provided within the immediate work area for emergency use.

If n-butyl mercaptan gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to n-butyl mercaptan, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If n-butyl mercaptan gets on the skin, wash it immediately with soap and water. If n-butyl mercaptan penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the location of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If n-butyl mercaptan is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing n-butyl mercaptan, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from n-butyl mercaptan vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing n-butyl mercaptan may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. n-Butyl mercaptan should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing n-butyl mercaptan may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for n-butyl mercaptan

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5 ppm	Any supplied-air respirator
	Any self-contained breathing apparatus
	Any chemical cartridge respirator with organic vapor cartridge(s)
Less than or equal to 12.5 ppm	Any supplied-air respirator operated in a continuous flow mode
	Any powered air-purifying respirator with organic vapor cartridge(s)
Less than or equal to 25 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
	Any powered air-purifying respirator with a tight-fitting facepiece and organic vapor cartridge(s)
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
Less than or equal to 500 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 1,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 1,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any suppplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 0.5 ppm (1.8 mg/m^3) (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-sec-BUTYLPHENOL

INTRODUCTION

This guideline summarizes pertinent information about o-sec-butylphenol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{14}O$

- **Structure**

$C_2H_5(CH_3)CHC_6H_4OH$

- **Synonyms**

2-(1-Methylpropyl)phenol; 2-sec-butylphenol

- **Identifiers**

1 CAS No.: 89-72-5

2. RTECS No.: SJ8920000

3. DOT UN: 2228 53

4. DOT label: St. Andrew's Cross

- **Appearance and odor**

o-sec-Butylphenol is a colorless, slightly volatile, combustible liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 150.2

2. Boiling point (760 mm Hg): 226° to 228°C (438.8° to 442°F)

3. Specific gravity (water = 1): 0.98 at 20°C (68°F)

4. Vapor density: Data not available

5. Melting point: 16°C (60.9°F)

6. Vapor pressure at 20°C (68°F): Data not available; however, o-sec-butylphenol is reported to be slightly volatile.

7. Solubility: Insoluble in water; soluble in alcohol, ether, and alkalies

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: None known

3. Hazardous decomposition products: Toxic gases may be released in a fire involving o-sec-butylphenol.

4. Special precautions: None known

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to o-sec-butylphenol; other sources report that this substance is combustible but does not ignite readily.

1. Flash point: 107.2°C (225°F)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or alcohol to fight fires involving o-sec-butylphenol.

Fires involving o-sec-butylphenol should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of o-sec-butylphenol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not

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possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving o-sec-butylphenol. Chemical protective clothing that is specifically recommended for o-sec-butylphenol may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by o-sec-butylphenol.

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for o-sec-butylphenol is 5 ppm (30 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (30 mg/m^3) as an 8-hr TWA with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned o-sec-butylphenol a threshold limit value (TLV) of 5 ppm (31 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to o-sec-butylphenol [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of eye and respiratory irritation and skin burns associated with exposure to o-sec-butylphenol.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to o-sec-butylphenol can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: o-sec-Butylphenol is an irritant of the eyes, skin, and upper respiratory tract. Application of 0.05 mg of o-sec-butylphenol to the eyes of rabbits caused severe injury [NIOSH 1991; ACGIH 1991a]. When applied to the skin of rabbits for 24 hr, 500 mg caused severe burns [ACGIH 1991a; NIOSH 1991]. The dermal LD_{50} in guinea pigs is 600 mg/kg [NIOSH 1991]. Rats survived a 7-hr exposure to an atmosphere saturated with o-sec-butylphenol vapor [ACGIH 1991a]. The oral LD_{50} is 2,700 mg/kg in rats and 600 mg/kg in guinea pigs [NIOSH 1991]. This material was nonmutagenic when tested in five strains of *Salmonella typhimurium* [NLM 1991].

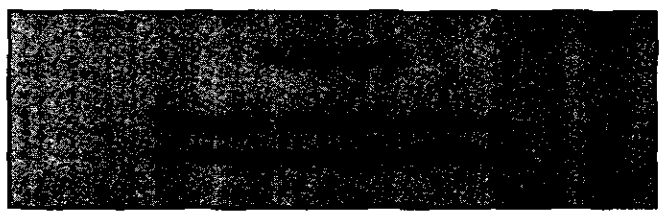
2. *Effects on Humans*: o-sec-Butylphenol is an eye, skin, and respiratory tract irritant and a potential corrosive. Acute occupational exposures to unspecified concentrations of this substance cause mild respiratory tract irritation, and prolonged skin contact results in dermal ulcerations and burns [ACGIH 1991a; NLM 1991]. Ingestion of a solution exceeding 5% o-sec-butylphenol may cause oral burns, which can become necrotic several days later [NLM 1991]. Using analogous data from other phenolic compounds, it may also cause nausea, vomiting, intense sweating, diarrhea, methomoglobinemia, tachycardia, hypotension, arrhythmias, seizures, CNS depression, hepatic injury, and death from respiratory arrest [NLM 1991].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to o-sec-butylphenol can cause eye irritation, redness, and pain; irritation of the nasal and respiratory tract mucosa; scratchy throat; and redness, swelling, and chemical burns of the skin.

2. *Chronic exposure*: Other than irritation, no signs or symptoms of chronic exposure to o-sec-butylphenol have been reported.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure*: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of o-sec-butylphenol! ***Immediately but gently***

flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If vapors, mists, or aerosols of o-sec-butylphenol are inhaled, move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if o-sec-butylphenol or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The preparation of plasticizers, resins, surface-active agents, and other products may involve o-sec-butylphenol and may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to o-sec-butylphenol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. *Chicago, IL: National Safety Council.*

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to o-sec-butylphenol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using

the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-sec-butylphenol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-sec-butylphenol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-sec-butylphenol on the respiratory tract and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for o-sec-butylphenol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-sec-butylphenol is determined by using a XAD-7 tube (100/50-mg sections; 15/50 mesh). Samples are collected at a recommended flow rate of 0.1 liter/min until a recommended air volume of 10 liters is collected. Analysis is conducted by high-performance liquid chromatography using ultraviolet light. This method is described in the OSHA Computerized Information System [OSHA 1989] and in the OSHA Laboratory In-House Methods File [OSHA 1990].

PERSONAL HYGIENE

Because o-sec-butylphenol can be absorbed through the skin in toxic amounts, workers should immediately and thoroughly wash with soap and water any areas of the skin that have contacted this substance.

Clothing and shoes contaminated with o-sec-butylphenol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of o-sec-butylphenol, particularly its potential for being an irritant and for being absorbed through the skin in toxic amounts.

A worker who handles o-sec-butylphenol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where o-sec-butylphenol or a solution containing it is handled, processed, or stored.

STORAGE

o-sec-Butylphenol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-sec-butylphenol should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained o-sec-butylphenol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-sec-butylphenol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.

5. Absorb liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

o-sec-Butylphenol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of o-sec-butylphenol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-sec-butylphenol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-sec-butylphenol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-sec-butylphenol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with o-sec-butylphenol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-sec-butylphenol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-sec-butylphenol.

If o-sec-butylphenol is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-sec-butylphenol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-sec-butylphenol. Contact lenses should not be worn if the potential exists for o-sec-butylphenol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR p-tert-BUTYLTOLUENE

INTRODUCTION

This guideline summarizes pertinent information about p-tert-butyltoluene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{11}H_{16}$

- *Synonyms*

1-Methyl-4-tert-butylbenzene; 1-tert-butyl-4-methylbenzene; 4-tert-butyltoluene; 1-(1,1-dimethyl)-4-methylbenzene; p-methyl-tert-butylbenzene; TBT; p-TBT

- **Identifiers**

1. CAS No.: 98-51-1
2. RTECS No.: XS8400000
3. DOT UN (for butyltoluenes): 2667 27
4. DOT label (for butyltoluenes): St. Andrew's Cross

- **Appearance and odor**

p-tert-Butyltoluene is a clear, colorless, combustible liquid with a gasoline-like odor. The odor threshold is reported to be 5 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 148.3
2. Boiling point (at 760 mm Hg): 192.8°C (379°F)
3. Specific gravity (water = 1): 0.86 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of p-tert-butyltoluene): 4.6
5. Melting point: −55°C (−67°F)
6. Vapor pressure at 25°C (77°F): 0.65 mm Hg
7. Solubility: Insoluble in water; slightly soluble in alcohol; very soluble in ether; miscible with most common industrial solvents
8. Evaporation rate (butyl acetate = 1): Very low

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Fires and explosions may result from contact of p-tert-butyltoluene with oxidizing materials.
3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released when p-tert-butyltoluene decomposes.
4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to p-tert-butyltoluene. Other sources rate p-tert-butyltoluene's fire hazard as moderate.

1. Flash point: 68°C (155°F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use carbon dioxide, dry chemical, foam, or water fog to fight fires involving p-tert-butyltoluene. Do not use a solid stream of water because the stream will scatter and spread the fire.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

EXPOSURE LIMITS

• OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for p-tert-butyltoluene is 10 ppm (60 mg/m^3) as an 8-hr time-weighted average (TWA) concentration and 20 ppm (120 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (60 mg/m^3) as an 8-hr TWA and 20 ppm (120 mg/m^3) as a STEL [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned p-tert-butyltoluene a threshold limit value (TLV) of 10 ppm (61 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek, and a STEL of 20 ppm (121 mg/m^3) for periods not to exceed 15 min [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of irritation, nausea, and central nervous system and cardiovascular effects associated with exposure to p-tert-butyltoluene.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to p-tert-butyltoluene can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals*: p-tert-Butyltoluene is a mild eye, skin, and respiratory tract irritant and a central nervous system depressant in animals acutely exposed; chronic exposure causes lung, brain, liver, and kidney damage. p-tert-Butyltoluene caused slight and transient eye irritation in rats and mild skin irritation in rabbits [NIOSH 1991; Grant 1986]. The dermal LD_{50} in rabbits is 19,600 mg/kg, and the LC_{50} in rats is 934 ppm for 1 hr [NIOSH 1991]. The oral LD_{50} in rats is 1,800 mg/kg. Acutely poisoned animals showed signs of eye and respiratory tract irritation and central nervous system effects including convulsions before death [Hine et al. 1954]. Rats repeatedly inhaling 25 or 50 ppm for 1 to 7 hr showed an increase in hemoglobin and a decrease in both erythrocyte and leukocyte counts [Clayton and Clayton 1981]. Repeated exposure of rats to 50 ppm caused liver and kidney changes and lesions of the brain and spinal cord [Hine et al. 1954]. Rats repeatedly exposed to 850 ppm for 1 hr progressively showed tremor, clonic movements, and flexor paralysis; pulmonary edema and pneumonia were the most frequent causes of death in animals after 10 such exposures [NLM 1990].

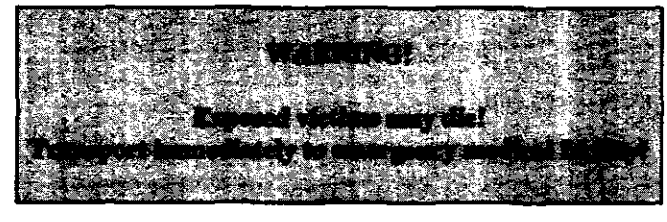
2. *Effects on Humans*: p-tert-Butyltoluene causes eye, skin, and upper respiratory tract irritation and central nervous system effects in humans. The irritant dose for the human eye is 5 ppm for 2 hr [NIOSH 1991]. The lowest acute toxic concentration in humans is 20 ppm for 5 min; central nervous system effects are seen at this concentration. Volunteers exposed for 5 min to p-tert-butyltoluene at concentrations ranging from 5 to 160 ppm reported experiencing nausea, upper respiratory tract irritation, and a metallic taste in the mouth. Volunteers exposed to the 160-ppm concentration became giddy and had increased pulse rates [Hine et al. 1954]. Workers chronically exposed to concentrations that were generally below 10 ppm reported anxiety and experienced decreased blood pressure, increased pulse rate, tremor, hematologic changes, and skin irritation [Hine et al. 1954].

• Signs and symptoms of exposure

1. *Acute exposure*: Acute exposure to p-tert-butyltoluene can cause contact irritation, runny nose, scratchy throat, headache, tiredness, giddiness, anxiety, nausea, metallic taste, weakness, tremor, ataxia, increased pulse rate, decreased blood pressure, dizziness, confusion, hallucinations, dysarthria, convulsions, dyspnea, increased breathing effort, temporary loss of consciousness, and death from possible respiratory failure [NLM 1990].

2. *Chronic exposure*: Repeated or prolonged contact of p-tert-butyltoluene causes defatting and irritation of the skin. It can also cause tremor, decreased blood pressure, elevated pulse rate, and blood changes.

• Emergency procedures



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Tissue irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of p-tert-butyltoluene. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Skin irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: If vapors, mists, or aerosols of p-tert-butyltoluene are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose to remove residues from nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if p-tert-butyltoluene or a solution containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve p-tert-butyltoluene and may result in worker exposures to this substance:

—Production of resins

—Use of p-tert-butyltoluene as a primary intermediate and as a solvent in the chemical and pharmaceutical industries

The following methods are effective in controlling worker exposures to p-tert-butyltoluene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to p-tert-butyltoluene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, respiratory system, blood, and central nervous system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to p-tert-butyltoluene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable

medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, respiratory system, blood, or central nervous system diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to p-tert-butyltoluene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of p-tert-butyltoluene on the eyes, skin, respiratory system, blood, and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for p-tert-butyltoluene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to p-tert-butyltoluene may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne p-tert-butyltoluene is determined by using charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 29 liters is collected. The samples are desorbed with carbon disulfide. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.001 to 0.01 mg per sample. This method is described in Method No. 1501 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If p-tert-butyltoluene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, followed by washing with soap and water.

Clothing and shoes contaminated with p-tert-butyltoluene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of p-tert-butyltoluene, particularly its potential for causing irritation of the eyes and skin.

A worker who handles p-tert-butyltoluene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where p-tert-butyltoluene or a solution containing p-tert-butyltoluene is handled, processed, or stored.

STORAGE

p-tert-Butyltoluene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [*29 CFR 1910.1200*]. The storage area must meet *OSHA* requirements for a Class IIIA flammable liquid [29 CFR 1910.106]. Ventilation fans and other electrical service must be of explosionproof design. Containers of p-tert-butyltoluene should be protected from physical damage and should be stored separately from oxidizers, heat, sparks, and open flame. Containers of p-tert-butyltoluene should be routinely inspected for leaks. To prevent static sparks, metal containers and equipment must be grounded and bonded during transfers. Because containers that formerly contained p-tert-butyltoluene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving p-tert-butyltoluene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.

5. Use water spray to reduce vapors, but be aware that the spray may not prevent ignition in closed spaces.

6. Use only nonsparking tools for cleanup.

7. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the p-tert-butyltoluene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

p-tert-Butyltoluene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of p-tert-butyltoluene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of p-tert-butyltoluene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although p-tert-butyltoluene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of p-tert-butyltoluene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with p-tert-butyltoluene. Gloves, aprons, boots, and other protective clothing and equipment should be used as necessary to prevent skin contact. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against

permeation by p-tert-butyltoluene and have demonstrated good-to-excellent resistance for periods greater than 8 hr: polyvinyl alcohol and Viton®. Nitrile rubber may withstand permeation for more than 4 but fewer than 8 hr. Butyl rubber, natural rubber, and neoprene have demonstrated poor resistance to permeation by p-tert-butyltoluene.

If p-tert-butyltoluene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which p-tert-butyltoluene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with p-tert-butyltoluene. Contact lenses should not be worn if the potential exists for exposure to p-tert-butyltoluene.

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Occupational Health Guideline for Cadmium Dust (as Cadmium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all cadmium dust. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Cadmium metal dust

- Formula: Cd
- Synonyms: None
- Appearance and odor: Odorless, gray powder.

Cadmium oxide dust

- Formula: CdO
- Synonyms: None
- Appearance and odor: Odorless, brown solid or blue-black solid.

Cadmium sulfide dust

- Formula: CdS
- Synonyms: Greenockite
- Appearance: Yellow-orange solid.

Cadmium chloride dust

- Formula: $CdCl_2$
- Synonyms: None
- Appearance: White solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cadmium dust is 0.2 milligram of cadmium dust per cubic meter of air (mg/m^3) averaged over an eight-hour work shift, with a ceiling level of 0.6 mg/m^3. NIOSH has recommended that the permissible exposure limit be reduced to 40 micrograms of cadmium per cubic meter of air ($\mu g/m^3$) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 200 $\mu g/m^3$ averaged over a 15-minute period. The recommendations in this guideline supplement the recommendations in the NIOSH Criteria Document for Cadmium, which should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cadmium dust can affect the body if it is inhaled. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Cadmium dust may cause irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath, and weakness. Death may occur. Ingestion of cadmium dust may cause nausea, vomiting, diarrhea, and abdominal cramps.

2. Long-term Exposure: Repeated or prolonged exposure to cadmium dust may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphysema), kidney damage, and mild anemia. Exposure to cadmium has also been reported to cause an increased incidence of cancer of the prostate in man. Injections of cadmium sulfate in animals have been reported to cause malformation in their offspring.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cadmium dust.

- **Recommended medical surveillance**

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

The following medical procedures should be made available to each employee who is exposed to cadmium dust at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, liver, kidneys, prostate, and blood should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to cadmium, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. In addition, the urine should be examined for low molecular weight proteins by use of 3% sulfosalicylic or other acceptable techniques.

—14" x 17" chest roentgenogram: Cadmium causes human lung damage. Surveillance of the lungs is indicated.

—Liver function tests: Cadmium may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—FVC and FEV (1 sec): Cadmium is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease. Urine protein measurements should be made available every four months.

• Summary of toxicology

Cadmium dust causes both acute and chronic effects. It is less toxic than cadmium fume, because dust has a larger particle size than fume; at high concentrations of the dust, physiologic effects similar to those arising from fume exposure could be expected. The acute effects primarily involve the lungs but may also affect other organ systems. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m³ for 1 hour, or 9 mg/m³ for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m³, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristical nasopharyngeal irritation followed by a feeling of chest constriction or substernal pain, with persistent cough and dyspnea; there may also be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop and progress rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. Cyanosis may be intense. In about 20% of the cases the dyspnea is progressive, accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days after exposure; at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Absorbed cadmium is retained to a large extent by the body, and excretion is very slow. Continued exposure to low levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of an emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of water, beans, and rice contaminated with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; severe pain in the back and joints, a waddly gait, osteomalacia, spontaneous fractures, and occasional fatal renal failure are characteristics of the disorder, which has been termed "itai-itai." Subcutaneous injection of cadmium metal suspended in fowl serum produced rhabdomyosarcomata in rats; cadmium sulfate in sterile distilled water produced sarcomata; and cadmium chloride solution produced pleomorphic sarcomata at the injection site. Increased incidence of prostatic cancer has been reported following occupational exposure to cadmium. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring; acute necrosis of rat testes follows large doses orally or parenterally, but testicular effects have not been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Cadmium metal dust**

1. Molecular weight: 112.4
2. Boiling point (760 mm Hg): 767 C (1412 F)
3. Specific gravity (water = 1): 8.642
4. Vapor density (air = 1 at boiling point of cadmium metal dust): Not applicable
5. Melting point: 321 C (609 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Cadmium oxide dust**

1. Molecular weight: 128.4
2. Boiling point (760 mm Hg): 900 C (1652 F) (sublimes and decomposes)
3. Specific gravity (water = 1): 6.95 or 8.15
4. Vapor density (air = 1 at boiling point of cadmium oxide dust): Not applicable
5. Melting point: 900 C (1652 F) (sublimes and decomposes)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0005
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Cadmium sulfide dust**

1. Molecular weight: 144.5
2. Boiling point (760 mm Hg): Sublimes in N_2 at 980 C (1796 F)
3. Specific gravity (water = 1): 4.82
4. Vapor density (air = 1 at boiling point of cadmium sulfide dust): Not applicable
5. Melting point: 1750 C (3182 F) at 100 atm.
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0001
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Cadmium chloride dust**

1. Molecular weight: 183
2. Boiling point (760 mm Hg): 960 C (1760 F)
3. Specific gravity (water = 1): 4.047
4. Vapor density (air = 1 at boiling point of cadmium chloride dust): Not applicable
5. Melting point: 568 C (1054 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 140
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of cadmium metal dust with strong oxidizers or with elemental sulfur, selenium, and tellurium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as cadmium oxide fume) may be released in a fire involving cadmium dust.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: 250 C (482 F) (layer) (cadmium metal dust)
3. Minimum explosive dust concentration: Data not available
4. Extinguishant: Dry powder for metal fires

- **Warning properties**

Grant states that "cadmium is a very toxic metal which gives off fumes when burned or heated strongly. Characteristically these fumes cause dryness and irritation of the throat, followed in a few hours by nausea and diarrhea. Smarting of the eyes occurs relatively infrequently, and no injury to the eyes of human beings has been reported. Neither eye nor respiratory irritation is enough to prevent exposures which may cause serious systemic poisoning and damage to the lungs."

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of cadmium dust. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of cadmium dust on a filter, followed by treatment with nitric acid, solution in hydrochloric acid, and atomic absorption spectrophotometric analysis. An analytical method for cadmium dust is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• If employees' clothing has had any possibility of being contaminated with cadmium dust, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with cadmium dust should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cadmium dust from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cadmium dust, the person performing the operation should be informed of cadmium dust's hazardous properties.

• Employees should be provided with and required to use dust-resistant safety goggles where there is any possibility of cadmium chloride dust contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to cadmium chloride dust, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Workers subject to skin contact with cadmium dust should wash with soap or mild detergent and water any areas of the body which may have contacted cadmium dust at the end of each work day.

• Eating and smoking should not be permitted in areas where cadmium dust is handled, processed, or stored.

• Employees who handle cadmium dust should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cadmium dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fabrication of cadmium-plated marine, aircraft, and motor vehicle equipment for corrosion-resistant coatings	Local exhaust ventilation; personal protective equipment
Liberation during processing of cadmium metal	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation in synthesis of cadmium compounds	Process enclosure; local exhaust ventilation
Liberation in manufacture and fabrication of cadmium alloys; recovery from flue dusts during smelting of lead and zinc operations	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of nuclear reactor rods	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If cadmium dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If cadmium dust gets on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands well before eating or smoking and at the close of work.

• **Breathing**

If a person breathes in large amounts of cadmium dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When cadmium dust or liquids containing cadmium dust have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the

person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.

• If cadmium dust is released in hazardous concentrations, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of release.
3. Collect released material in the most convenient and safe manner for reclamation or for disposal in sealed conainers in a secured sanitary landfill.

• Waste disposal method:

Cadmium dust may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 11, 1976.

RESPIRATORY PROTECTION FOR CADMIUM DUST (AS CADMIUM)

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m³
Dust Concentration	
1 mg/m³ or less	Any dust respirator, except single-use.
2 mg/m³ or less	Any dust respirator, except single-use or quarter-mask respirator. Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
10 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Cadmium Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Cd/CdO
- Synonyms: None
- Appearance: Finely divided solid particles dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cadmium fume is 0.1 milligram of cadmium fume per cubic meter of air (mg/m³) averaged over an eight-hour work shift, with an acceptable ceiling level of 0.3 mg/m³. NIOSH has recommended that the permissible exposure limit be reduced to a time-weighted average of 40 micrograms cadmium per cubic meter (ug/m³) with a ceiling level of 200 ug cadmium/m³ for a 15-minute period. The NIOSH Criteria Document for Cadmium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cadmium fume can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Cadmium fume causes irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath, and weakness. Death may occur.

2. Long-term Exposure: Repeated or prolonged exposure to cadmium fume may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphysema), kidney damage, and mild anemia. Exposure to cadmium fume has also been reported to cause an increased incidence of cancer of the prostate in men. Injections of cadmium sulfate in animals have been reported to cause malformation in their offspring. This effect has not been reported in humans.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cadmium fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cadmium fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, kidneys, and blood should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to cadmium, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The urine should be examined for the specific protein.

—14" x 17" chest roentgenogram: Cadmium causes human lung damage. Surveillance of the lungs is indicated.

—Liver function tests: Cadmium may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—FVC and FEV (1 sec): Cadmium is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
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U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Urine protein measurements should be made available every four months.

• **Summary of toxicology**

Cadmium fume (cadmium oxide) is a severe pulmonary irritant that has caused fatal pulmonary edema in workers; chronic exposures may lead to severe pulmonary emphysema. Cadmium sulfide produces malignant tumors in animals by injection, suggesting that cadmium is carcinogenic. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m³ for 1 hour, or 9 mg/m³ for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m³, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristically nasopharyngeal irritation, followed by a feeling of chest constriction or substernal pain, with cough and dyspnea; there also may be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. In about 20% of the cases the dyspnea is progressive, accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days of exposure; at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Continued exposure to lower levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with evidence of renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. Cadmium absorbed by any route is, to a very large extent, retained by the body. Excretion is very slow. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of beans, rice and water contaminated with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; pain in the back and joints, an unsteady gait, osteomalacia, bone fractures, and occasional renal failure are characteristics of the disorder. Rats, injected subcutaneously with cadmium metal suspended in fowl serum, produced rhabdomyosarcomata; with cadmium sulfate in sterile distilled water, sarcomata; and with cadmium chloride solution, pleomorphic sarcomas at the injection site, suggesting that cadmium is carcinogenic. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring. Increased prostatic and lung cancer has been reported in humans exposed to cadmium oxide. Acute necrosis of the rat testis follows large doses orally or parenterally.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 112— 128
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of cadmium fume): Not applicable
5. Melting point: Not applicable
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Not applicable

• **Flammability**

1. Not applicable

• **Warning properties**

Grant reports that "smarting of the eyes occurs relatively infrequently (upon exposure to cadmium fume), and no injury to the eyes of human beings has been reported. Neither eye nor respiratory tract irritation is enough to prevent exposures which may cause serious systemic poisoning and damage to the lungs."

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

airborne concentrations of cadmium fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of cadmium fume on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for cadmium fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

SANITATION

• Eating and smoking should not be permitted in areas where fumes may be generated in the handling or processing of cadmium.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cadmium fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during smelting and refining of ores where it is a by-product of zinc, lead, and copper-bearing ores	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during recovery of metal by processing of scrap; during melting and pouring of cadmium metal; during casting of alloys for cadmium-copper, cadmium-lead, cadmium-bismuth, cadmium-silver, cadmium-nickel, cadmium-lead-silver, cadmium-lead-silver-nickel, cadmium-lead-bismuth-tin, and cadmium-gold products used for coating telephone cables, trolley wires, welding electrodes, automatic sprinkling systems, steam boilers, fire alarms, high-pressure/temperature bearings, starting switches, aircraft relays, light-duty circuit breakers, low-temperature solder, and jewelry	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during fabrication of metal, alloys, or plated steel	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during casting and use of solders; during melting of cadmium ingots for paint and pigment manufacture used for coloring of plastics and ceramic glazes, electroplating, and in chemical synthesis	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during coating on metals by hot dipping or spraying	Process enclosure; local exhaust ventilation; personal protective equipment

Liberation during manufacture of nickel-cadmium batteries for use in radio-portable telephones, convenience appliances, and vented cells used in air planes, heliocopters, and stand-by power and lighting	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Breathing**

If a person breathes in large amounts of cadmium fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.

• If potentially hazardous amounts of cadmium fume are inadvertently released, ventilate the area of the release to disperse the fume.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 11, 1976.

RESPIRATORY PROTECTION FOR CADMIUM FUME

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
1 mg/m³ or less	Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

DHHS (NIOSH) Publication No. 88-118, Supplement I-OHG

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer
Cincinnati, Ohio

1988

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

NOTE TO THE READER

These 35 occupational safety and health guidelines are being published to disseminate technical information about chemical hazards to workers, employers, and occupational safety and health professionals. Each guideline includes data on chemical names and synonyms, chemical and physical properties, exposure limits, signs and symptoms of exposure, as well as recommendations for medical monitoring, respiratory and personal protective equipment, and control procedures. These recommendations reflect good industrial hygiene and medical monitoring practices, and their implementation should help employers achieve a sound occupational health program.

The recommendations and information contained in these guidelines may be superseded as new information becomes available; readers are advised to regard these recommendations as general guidelines and should not rely on them for achieving compliance with occupational safety and health regulations.

This document supplements the 1981 publication entitled NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards (Washington, DC: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, DHHS [NIOSH] Publication No. 81-123). Readers may wish to insert each guideline at the appropriate place in that 3-volume set.

CONTENTS

2-Acetylaminofluorene

Acrylonitrile

Aldrin

4-Aminodiphenyl

Arsenic, Inorganic

Arsine

Asbestos

Benzidine

Benzyl Chloride

Carbon Black

bis-Chloromethyl Ether

Chloromethyl Methyl Ether

Cotton Dust

DDT

Dieldrin

Di-2-Ethylhexyl Phthalate

4-Dimethylaminoazobenzene

1,1-Dimethylhydrazine

Ethylene Dichloride

Ethylene Oxide

Furfuryl Alcohol

Hydrazine

Hydroquinone

Lead, Inorganic

Methyl Mercaptan

Monomethyl Hydrazine

Nitroglycerin and Ethylene Glycol Dinitrate

N-Nitrosodimethylamine

2-Pentanone

Phenylhydrazine

beta-Propiolactone

Tetramethyl Succinonitrile

Toluene Diisocyanate

Trichloroethylene

Vinyl Chloride

OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

DHHS (NIOSH) Publication No. 89-104, Supplement II-OHG

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
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NOTICE

The guidelines in Supplement I are not packaged in the exact order listed in the contents. Please add them to your notebook binders in alphabetical order, as indicated in the table of contents.

CONTENTS

Acetone
Allyl Glycidyl Ether
Antimony and Its Compounds
Benzene
Beryllium and Its Compounds
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Cresol, All Isomers
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Hexone
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Mesityl Oxide
Methyl (n-Amyl) Ketone
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beta-Naphthylamine
4-Nitrobiphenyl
2-Nitropropane
Phenyl Glycidyl Ether

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM CARBONATE

INTRODUCTION

This guideline summarizes pertinent information about calcium carbonate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaCO_3$

- **Synonyms**

  Aragonite, agricultural limestone, agstone, Bell mine pulverized limestone, calcite, chalk, domolite, franklin, limestone, lithographic stone, marble, Portland Stone, Sohnhofen stone

- **Identifiers**

  1. CAS No.: 1317-65-3
  2. RTECS No.: EV9580000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium carbonate is a noncombustible, odorless, white powder or colorless crystalline solid. Calcium carbonate occurs naturally in the minerals aragonite, calcite, limestone, marble, and vaterite. The two natural forms of calcium carbonate that are important commercially are aragonite and calcite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 100.09
  2. Boiling point: Not applicable
  3. Specific gravity at 20°C (68°F) (water = 1): 2.83 (aragonite); 2.71 (calcite)
  4. Vapor density: Not applicable
  5. Melting point: 825°C (1,517°F) (aragonite); 1,339°C (2,442°F) (calcite)
  6. Vapor pressure: Not applicable
  7. Solubility: Insoluble in water and alcohol; soluble in dilute acids.
  8. Evaporation rate: Not applicable

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
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National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Reactivity

1. Conditions contributing to instability: None

2. Incompatibilities: Contact of calcium carbonate with acids, alum, ammonium salts, or mercury and hydrogen causes a reaction, and contact with fluorine causes ignition.

3. Hazardous decomposition products: Toxic particulates (such as calcium oxide) may be released in a fire involving calcium carbonate.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium carbonate; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium carbonate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium carbonate.

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium carbonate is 15 mg/m^3 of air (total dust) and 5 mg/m3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium carbonate a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to calcium carbonate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium carbonate can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Calcium carbonate causes moderate-to-severe irritation in contact with the tissues of animals. Instilled into rabbits' eyes, calcium carbonate caused severe irritation [NIOSH 1991]. In contact with the skin of rabbits for 24 hr, this substance caused moderate irritation [NIOSH 1991]. The oral LD_{50} in rats is 6,450 mg/kg [NIOSH 1991].

2. *Effects on Humans:* Calcium carbonate dust is a physical irritant of the eyes, nose, mucous membranes, and skin of humans. Contact of calcium carbonate dust with the eyes causes redness, pain, and inflammation of the eyelids while contact with the skin causes local irritation of moderate degree [NLM 1991]. Exposure to large amounts of the dust of this substance causes coughing, sneezing, and nasal irritation [NLM 1991]. Although chronic exposure to pure calcium carbonate does not cause pneumoconiosis, similar exposure to impure limestone (calcium carbonate) containing 3% to 20% quartz may pose a silicosis risk [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Overexposure to calcium carbonate

dust can cause irritation of the eyelids; redness, tearing, and pain in the eyes; runny nose; sneezing; and coughing. Contact with the skin causes dryness and irritation.

2. *Chronic exposure:* Although no signs or symptoms of chronic exposure to calcium carbonate have been reported, quartz contamination of limestone in excess of 2% may pose a silicosis risk.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium carbonate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** induce vomiting if calcium carbonate has been mixed with a petroleum distillate such as kerosene or diesel fuel.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve calcium carbonate and may result in worker exposures to this substance:

—Use as a neutralizing agent, filler, and extender in rubber, plastic, and paint products, and as an opacification agent in paper products

—Use in the manufacture of putty, tooth powders, antacids, whitewash, quicklime, Portland cement, dentifrices, ceramics, polishes, insecticides, inks, shoe dressings, foods, cosmetics, pharmaceuticals, antibiotics, adhesives, matches, pencils, crayons, linoleum, welding rods, and insulating compounds

—Use in removing sulfur dioxide from stack gases and as a metallurgical flux

—Use in analytical chemistry to detect and measure halogens in organic combinations and in the laboratory generation of carbon dioxide

—Use as a pigment and as a source of lime

—Use in human and veterinary medicine as an antacid.

—As a dietary supplement, as a nutrient, and as an antidiarrheal agent

The following methods are effective in controlling worker exposures to calcium carbonate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to toxic substances should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to calcium carbonate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium carbonate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium carbonate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium carbonate on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium carbonate.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the

time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

The OSHA method for determining worker exposures to airborne concentrations of calcium carbonate (total dust) is made using a tared, low-ash polyvinyl chloride filter (LAPCF) with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System as Dust, Total [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1987]. NIOSH has a similar method (Method 0500) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984a] which also involves gravimetric analysis. In the NIOSH method, samples are collected at a flow rate of 1.5 to 2 liters/min. The minimum sample volume for an airborne concentration of 15 mg/m^3 is 15 liters, and the maximum is 133 liters. The overall precision for the NIOSH method is 0.056.

The OSHA method for determining worker exposures to airborne concentrations of calcium carbonate (respirable fraction) is made using a tared, low-ash polyvinyl chloride filter (LAPCF) with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is held in a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 800 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System as Dust (Respirable Nuisance) [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1987]. NIOSH has a similar method (Method 0600) in the *NIOSH Manual of Analytical Methods* [NIOSH 1984b], which also involves gravimetric analysis. In the NIOSH method, samples are collected at a flow rate of 1.7 liter/min. The minimum sample volume for an airborne concentration of 5 mg/m^3 is 75 liters, and the maximum is 1,000 liters. The overall precision for the NIOSH method ranges from 0.043 to 0.145 in laboratory tests and from 0.144 to 0.227 in field tests.

PERSONAL HYGIENE

If calcium carbonate collects on the skin in large quantities, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium carbonate should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium carbonate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium carbonate is handled, processed, or stored.

STORAGE

Calcium carbonate should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of calcium carbonate should be protected from physical damage and should be stored separately from acids, alum, ammonium salts, fluorine, mercury, hydrogen, heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a major spill involving calcium carbonate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a major spill:

1. For small spills, vacuum or wet down the spilled material and place into waste containers for disposal.

2. For large spills, wet down the material and dike for later disposal.

3. To the extent feasible, avoid generating dust during cleanup.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

Emergency planning requirements

Calcium carbonate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

Reportable quantity requirements for hazardous releases

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium carbonate; there is no reportable quantity for this substance.

Community right-to-know requirements

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium carbonate emitted or released from their facility annually.

Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21–261.24. Although calcium carbonate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium carbonate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with calcium carbonate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to calcium carbonate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium carbonate.

If calcium carbonate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which calcium carbonate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium carbonate. Contact lenses should not be worn if the potential exists for calcium carbonate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM CYANAMIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium cyanamide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaCN_2$

- **Structure**

  Ca:NCN

- **Synonyms**

  Aero-cyanamid; cyanamide, calcium salt; aero cyanamid granular; calcium carbimide; aero cyanamid special grade; Alzodef; lime-nitrogen; nitrogen lime; nitrolim, nitrolime

- **Identifiers**

  1. CAS No.: 156-62-7
  2. RTECS No.: GS6000000
  3. DOT UN: 1403 40 (not hydrated, containing more than 0.1% calcium carbide)
  4. DOT label: None (not hydrated, containing more than 0.1% calcium carbide)

- **Appearance and odor**

  Calcium cyanamide is a noncombustible, colorless, gray, or black crystalline solid or powder. No information is available on the odor of this substance. The commercial grade may contain a small amount of calcium carbide, which may produce acetylene in closed containers and vessels.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 80.11
  2. Boiling point (760 mm Hg): Sublimes at 1,150° to 1,200°C (2,102° to 2,192°F)
  3. Specific gravity (water = 1): 2.29 at 20°C (68°F)
  4. Vapor density: Data not available
  5. Melting point: 1,340°C (2,444°F)
  6. Vapor pressure: Not volatile
  7. Solubility: Decomposes in water to liberate acetylene gas and ammonia
  8. Evaporation rate: Data not available

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Reactivity

1. Conditions contributing to instability: Moisture

2. Incompatibilities: Contact with any form of moisture (ice, steam, moist air, water) causes calcium cyanamide to decompose, liberating acetylene and ammonia. Contact with all solvents tested also causes calcium cyanamide to decompose.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving calcium cyanamide.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium cyanamide. In pure form, this substance is not combustible; however, the commercial product may contain calcium carbide, which may liberate very flammable gases and vapors on contact with moisture.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, soda ash, sand, or lime to fight fires involving calcium cyanamide. Do not use foam or water. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving calcium cyanamide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of calcium cyanamide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium cyanamide. Structural firefighters' protective clothing may not provide protection against permeation by calcium cyanamide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for calcium cyanamide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium cyanamide a threshold limit value (TLV) of 0.5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of irritation and vasomotor effects associated with exposure to calcium cyanamide [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium cyanamide can occur through inhalation, eye or skin contact, dermal absorption, or ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Calcium cyanamide can be a severe irritant of the eyes and skin in animals. In pure water or alkaline solutions, it may polymerize to dicyandiamide, a less toxic product. When instilled into rabbits' eyes, the dust of this material was quite irritating [ACGIH 1991]. When applied as a paste to the clipped skin of rabbits under occlusion for 24 hr, a 10-g/kg dose of calcium cyanamide killed two of five rabbits; all animals survived when the dosage was reduced to 5 g/kg [ACGIH 1991]. All surviving animals developed severe skin irritation several days

after application [ACGIH 1991]. In marked contrast to the previous data concerning rabbit dermal lethality, other investigators reported the dermal LD_{50} in rabbits to be 590 mg/kg [NIOSH 1991]. The lowest lethal concentration in rats is 86 mg/m^3 for 4 hr [ACGIH 1991]. The oral LD_{50} in rats is 158 mg/kg [NIOSH 1991]. Calcium cyanamide is mutagenic in bacterial test systems [NIOSH 1991; NLM 1992]. Rats and mice fed a diet containing 63 or 126 ppm (male rats), 63 or 252 ppm (female rats), or 315 or 1,260 ppm (male and female mice) of calcium cyanamide for 2 years failed to develop tumors that were treatment related at statistically significant levels; however, some of the mice did develop hemangiosarcomas of the circulatory system, lymphomas, and leukemia [ACGIH 1991].

2. *Effects on Humans:* Calcium cyanamide is a primary irritant and sensitizer of the eyes, skin, and mucous membranes. The dust of calcium cyanamide is a primary irritant that can induce skin ulcers and be caustic to the eyes [Clayton and Clayton 1981; NLM 1992]. Skin contact with this substance also causes skin sensitization in approximately 0.5% to 1% of exposed workers [ACGIH 1991]. Inhalation of the dust can cause rhinitis, pharyngitis, laryngitis, and tracheobronchitis. Nasal septal perforation has also been reported in chronically exposed workers. Workers exposed to calcium cyanamide at unspecified concentrations may develop miosis, salivation, lacrimation, and twitching plus a transient vasomotor disturbance that can cause skin and mucous membrane flushing, nausea, vomiting, headache, fatigue, vertigo, dyspnea, rapid breathing, and low blood pressure; in severe cases, shock, coma, and death may follow [ACGIH 1991; Gosselin et al. 1984; NLM 1992]. Attacks are usually transient, lasting for 30 min to 2 hr, and the ingestion of alcohol may precipitate or intensify this syndrome [Gosselin et al. 1984]. Although an oral dose of 571 mg/kg has proved fatal in humans, the estimated total lethal dose ranges from 20 to 50 grams [NIOSH 1991; NLM 1992]. However, death occurred within 1 hr when a patient drank ethanol following ingestion of 100 mg calcium cyanamide [NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium cyanamide can cause eye irritation, runny nose, sore throat, and coughing. Itchy, reddened skin, especially on the exposed areas of the body, has been reported; continued skin contact may cause skin burns. Inhalation exposure can produce respiratory tract irritation and may cause facial and upper-body flushing, accompanied by nausea, vomiting, headache, fatigue, vertigo, dyspnea, rapid breathing, a sense of oppression in the chest, and shivering. Low blood pressure, circulatory collapse, and coma may follow in more serious exposures. These symptoms may be triggered or intensified by alcohol ingestion, and a marked intolerance to alcoholic beverages can develop.

2. *Chronic exposure:* Calcium cyanamide may cause some individuals to develop skin sensitization, with raised, reddened, and itching areas of the skin (hives). Chronic rhinitis and nasal septal perforation have also been reported in workers exposed to the dust.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! Immediately, continuously, and gently wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium cyanamide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium cyanamide and may result in worker exposures to this substance:

—Use in the nitridation and desulfurization of steel

—Use as a raw material in the manufacture of dicyandiamide and calcium cyanide

—Use as a fertilizer and in the manufacture of nitrogen products

—Use in human medicine to treat alcoholism

—Used formerly as a defoliant, herbicide, and pesticide

The following methods are effective in controlling worker exposures to calcium cyanamide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for

exposure to calcium cyanamide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and on a history of allergies or alcohol intake. All potentially exposed workers should be warned of the adverse signs and symptoms associated with exposure to calcium cyanamide and the concomitant ingestion of alcohol.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium cyanamide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of alcohol intake or allergies and other findings consistent with skin diseases.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium cyanamide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium cyanamide on the skin (including allergic sensitization) and on any vasomotor episodes that have occurred. All workers should be reminded of the adverse effects associated with concomitant exposure to calcium cyanamide and the ingestion of alcohol. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium cyanamide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium cyanamide is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If calcium cyanamide contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with calcium cyanamide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium cyanamide, particularly its potential to cause irritation of the eyes and skin.

A worker who handles calcium cyanamide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium cyanamide or a solution containing calcium cyanamide is handled, processed, or stored.

STORAGE

Calcium cyanamide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled

in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium cyanamide should be protected from physical damage and should be stored separately from moisture, calcium carbide, heat, sparks, and open flame. Because containers that formerly contained calcium cyanamide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving calcium cyanamide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Prevent any contact of calcium cyanamide with water.
6. Use nonsparking tools and equipment for cleanup.
7. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium cyanamide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium cyanamide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of calcium cyanamide per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium cyanamide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium cyanamide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium cyanamide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with calcium cyanamide. Chemically resistant gloves, boots, aprons, and gauntlets are recommended to prevent contact of the skin with this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to permeation by calcium cyanamide. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium cyanamide.

Safety glasses, goggles, or face shields should be worn during operations in which calcium cyanamide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium cyanamide. Contact lenses should not be worn if the potential exists for calcium cyanamide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM HYDROXIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium hydroxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $Ca(OH)_2$

- **Synonyms**

  Bell mine, calcium hydrate, hydrated lime, caustic lime, Kemikal, slaked lime

- **Identifiers**

  1. CAS No: 1305-62-0
  2. RTECS No.: EW2800000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium hydroxide is a soft, white, powder or granule, noncombustible material with a bitter taste and no odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 74.1
  2. Boiling point (760 mm Hg): Decomposes at 580°C (1,076°F)
  3. Specific gravity (water = 1): 2.24 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: 580°C (1,076°F) (loses its water)
  6. Vapor pressure: Not applicable
  7. Solubility: Soluble in water, sugar or ammonium solutions, acids, and glycerol; insoluble in alcohol
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame
  2. Incompatibilities: Explosions may result from con-

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tact of calcium hydroxide with maleic anhydride, phosphorus, nitroethane, nitromethane, nitroparaffins, or nitropropane.

3. Hazardous decomposition products: Toxic particulates (such as calcium oxide) may be released in a fire involving calcium hydroxide.

ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium hydroxide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of irritation associated with exposure to calcium hydroxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium hydroxide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Calcium hydroxide is a corrosive that affects all tissues it contacts. Direct application of an aqueous 10% calcium hydroxide solution to the central corneal surface of rabbit eyes resulted in corrosion with persisting severe irritation beyond 21 days [NLM 1992]. The oral LD_{50}s in rats and mice are 7,340 and 7,300 mg/kg, respectively [NIOSH 1991]. The eyes of rabbits were severely affected by the application of 10 mg calcium hydroxide [Grant 1986; Sax and Lewis 1989]. Rats whose drinking water contained 50 or 350 mg calcium hydroxide/liter became restless and aggressive after 2 months and showed a loss in body weight, decreased phagocyte and erythrocyte counts, and decreased hemoglobin after 3 months on this regimen. Autopsy showed inflammation of the small intestines and dystrophic changes in the stomach, kidneys, and liver of these animals [Proctor et al. 1988].

2. *Effects on Humans:* Calcium hydroxide is a tissue corrosive and one of the most common causes of corrosive chemical eye burns. Direct contact of the skin with calcium hydroxide causes skin irritation and may also lead to corrosive chemical burns [Grant 1986; Clayton and Clayton 1981]. Because calcium hydroxide slowly penetrates the skin, the degree of damage is directly related to the degree and duration of exposure [NLM 1992]. Prolonged contact of the skin with calcium hydroxide may cause skin desquamation and a vesicular rash, skin ulceration, and corrosion in some cases [Parmeggiani 1983; NLM 1992]. Ingestion of this material has caused severe pain, vomiting, tissue corrosion, perforation, and death. Survivors may develop esophageal strictures [NLM 1992]. Chronic dermatitis can also be induced by repeated exposure to this alkali [NLM 1992]. Chronic inhalation of calcium hydroxide dust is reported to have caused bronchitis and pneumonia [Parmeggiani 1983].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium hydroxide can induce redness, tearing, irritation, or corrosion of the eyes; runny nose, upper respiratory tract irritation, bronchitis, and pneumonia; and redness, rashes, irritation, or corrosion of the skin.

2. *Chronic exposure:* Calcium hydroxide can cause chronic skin dermatitis, desquamation, vesiculation, and ulceration, as well as coughing, fluid in the lungs, and difficult breathing.

- **Emergency procedure**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash

skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium hydroxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium hydroxide and may result in worker exposures to this substance:

—Manufacture of medicinal antacids, fecal deodorants, polysaccharides, mortar, plaster, whitewash, cement, and other paving and building materials

—Use as an intermediate in the production of propylene oxide and calcium hypochlorite, as a flux in iron and steel manufacture, and as a buffering agent for metals, pearls, and celluloid

—Use in lubricants, drilling fluids, fertilizers, and pesticides

—Use to dehair hides

—Use in water softening and treatment and in water-based paints

—Use in fireproofing compounds, fireproof coatings, and in soil treatment

—Use as a scrubbing and neutralizing agent in the chemical industry

—Manufacture of calcium salts, causticizing soda, and depilatories

—Use in ammonia recovery, in gas manufacture, in paper pulp manufacture, in the purification of sugar juices, as a disinfectant, as an accelerator for low-grade rubber compounds, in petrochemicals, and as a shell-forming agent in the poultry industry

The following methods are effective in controlling worker exposures to calcium hydroxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to calcium hydroxide, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium hydroxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with skin or respiratory tract diseases.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium hydroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium hydroxide on the skin and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium hydroxide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium hydroxide is determined by using a mixed cellulose ester filter (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 480 liters is collected. The sample is then treated with water to extract the calcium hydroxide. Analysis is conducted by atomic absorption spectroscopy. This method has a sampling and analytical error of 0.28 and is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If calcium hydroxide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium hydroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium hydroxide, particularly its potential to cause skin burns.

A worker who handles calcium hydroxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium hydroxide or a solution containing calcium hydroxide is handled, processed, or stored.

STORAGE

Calcium hydroxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium hydroxide should be protected from physical damage and should be stored separately from acidic materials, maleic anhydride, nitroethane, nitromethane, nitropropane, nitroparaffins, phosphorus, heat, sparks, and open flame. Because containers that formerly contained calcium hydroxide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium hydroxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill to reduce dust concentration.
4. To the extent possible, avoid generating dust during cleanup.
5. For small spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium hydroxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium hydroxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium hydroxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium hydroxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium hydroxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with calcium hydroxide. Chemically resistant clothing, gloves, boots, and other protective clothing are recommended when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by calcium hydroxide and may provide protection for periods greater than 8 hr: natural rubber, nitrile rubber, and neoprene rubber. Polyvinyl chloride has also demonstrated good-to-excellent resistance when tested against calcium hydroxide.

Safety glasses, goggles, or face shields should be worn during operations in which calcium hydroxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium hydroxide. Contact lenses should not be worn if the potential exists for calcium hydroxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

Supplement III–OHG

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio

1992

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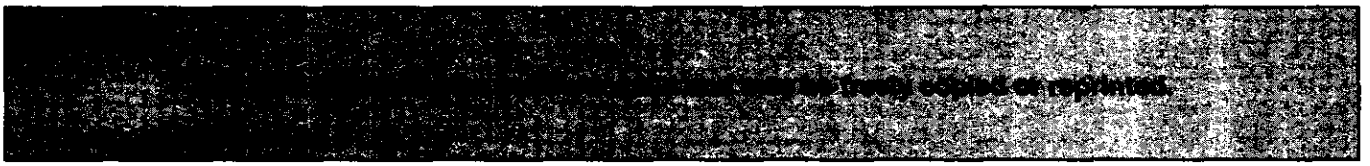

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DHHS (NIOSH) Publication No. 92–110, Supplement III–OHG

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NOTE TO THE READER

This document is the third in a series of supplements to the 1981 Publication *NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards* (Washington, DC: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, DHHS [NIOSH] Publication No. 81-123). The two previous supplements are as follows:

1. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 88-118, Supplement I-OHG). This document contains 35 guidelines.
2. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 89-104, Supplement II-OHG). This document contains 30 guidelines.

The 50 guidelines presented here in the third supplement include 33 revisions of previously issued guidelines and 17 new guidelines. Readers should replace the outdated guidelines in the original 1981 publication with the revised guidelines provided here.

The 50 occupational safety and health guidelines presented here are being published to disseminate technical information about chemical hazards to workers, employers, and occupational safety and health professionals. Each guideline includes (1) data on the chemical name and synonyms, chemical and physical properties, exposure limits, and signs and symptoms of exposure, and (2) recommendations for medical monitoring, personal protective equipment, and control procedures. These recommendations reflect good industrial hygiene and medical monitoring practices, and their implementation should help employers to achieve sound occupational health programs.

The recommendations and information in these guidelines may be superseded as new information becomes available; readers should therefore regard these recommendations as general guidelines and should not rely on them for achieving compliance with occupational safety and health regulations.

The first two supplements to the original guidelines can be ordered from the Superintendent of Documents (U.S. Government Printing Office, Washington, DC 20402-9325) or from the National Technical Information Service (5285 Port Royal Road, Springfield, VA 22161 [telephone: 703-487-4650]). The original three-volume set of guidelines is available only from the National Technical Information Service (NTIS). The stock numbers for the U.S. Government Printing Office (GPO) and NTIS are as follows:

Publication	*GPO No.*	*NTIS No.*
Volumes I, II, III (DHHS [NIOSH] Publication No. 81-123)	——	PB 83-154609
Supplement I-OHG (DHHS [NIOSH] Publication No. 88-118)	017-033-00439-1	PB 89-203129
Supplement II-OHG (DHHS [NIOSH] Publication No. 89-104)	017-033-00441-2	PB 89-203137

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM OXIDE

INTRODUCTION

This guideline summarizes pertinent information about calcium oxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CaO

- **Synonyms**

  Lime, burnt lime, calcia, calx, quicklime, pebble lime, unslaked lime

- **Identifiers**

  1. CAS No.: 1305-78-8
  2. RTECS No.: EW3100000
  3. DOT UN: 1910 60
  4. DOT label: None

- **Appearance and odor**

  Calcium oxide may take the form of odorless crystals, white or grayish-white lumps, or granular powder. The commercial material may have a yellowish or brownish tint because of its iron content.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 56.08
  2. Boiling point (760 mm Hg): 2,850°C (5,162°F)
  3. Specific gravity (water = 1): 3.32 to 3.35 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: 2,572°C (4,662°F)
  6. Vapor pressure at 20°C (68°F): 0 mm Hg
  7. Solubility: Soluble in water (forms slaked lime and generates a large quantity of heat); soluble in acids, glycerol, and sugar solution; practically insoluble in alcohol.
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Moisture

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2. Incompatibilities: Contact of calcium oxide with water causes a violent reaction, and the heat liberated during this reaction may cause the ignition of combustible substances. Calcium oxide reacts violently with ethanol, liquid hydrogen fluoride, some acids, some halogens, some metal halides, some metals, and some oxides, boron trifluoride, liquid hydrofluoric acid, phosphorus pentoxide, boric oxide and calcium chloride mixtures, fluorine, chlorine trifluoride, and carbon dioxide.

3. Hazardous decomposition products: Toxic particulates (such as particles of calcium hydroxide) may be released in a fire involving calcium oxide.

4. Special precautions: When exposed to air, this substance will react with the moisture and the carbon dioxide in the air. Calcium oxide swells when moist and may burst its containers.

Flammability

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) for calcium oxide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Calcium oxide will not burn. Because water reacts violently with calcium oxide, it should NOT be used as an extinguishant. Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium oxide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of calcium oxide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Do NOT allow water to come into contact with the contents of containers. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium oxide. Structural firefighters' protective clothing may provide limited protection against fires involving calcium oxide.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium oxide is 5 mg/m^3 as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium oxide a threshold limit value (TLV) of 2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of eye, skin, and respiratory tract irritation associated with exposure to calcium oxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium oxide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* No published data on the effects of calcium oxide exposure in animals were available for review.

2. *Effects on Humans:* Calcium oxide causes marked irritation and corrosion of contacted tissues. The irritant and corrosive effects of exposure to calcium oxide dust are primarily a result of its alkalinity and

its heat-generating reaction when in contact with moisture [Clayton and Clayton 1981]. Addition of water to calcium oxide has generated temperatures as high as 800°C (1,472°F) [NLM 1991]. In contact with the eyes, calcium oxide causes severe burns and may cause corneal ulceration [Grant 1986; Sittig 1985]. In contact with the skin, calcium oxide causes dermatitis or corrosive burns, with desquamation and a vesicular rash [Sittig 1985]. Inhalation of the dust at a concentration of 25 mg/m^3 caused marked nasal irritation in exposed workers; however, at a concentration of 9 or 10 mg/m^3, this effect disappeared [Clayton and Clayton 1981]. Exposure to calcium oxide at unspecified concentrations causes inflammation of the respiratory passages and ulceration and perforation of the nasal septum [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium oxide can produce spasmodic blinking, tears, and adhesion of calcium oxide particles to the eyeball and the conjunctival sac; dermatitis with desquamation and a vesicular rash, ulceration, and corrosive burns; and coughing, sneezing, and inflammation of the nose and throat, bronchitis, and pneumonia.

2. *Chronic exposure:* Calcium oxide has caused ulceration and perforation of the nasal septum and severe recurrent dermatitis.

- **Emergency procedures**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium oxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium oxide and may result in worker exposures to this substance:

—Use as raw material in the preparation of chlorinated lime, bleaching powder, and calcium salts and as a binding agent in the manufacture of Portland cement, mortar, stucco, plaster, bricks, refractory material, and glass

—Use as a softening, purifying, coagulating, and suspending compound in water treatment and purification; as a neutralizer of acid waste effluents; to remove sulfur dioxide from stack gases; to treat sewage and waste from steel fabrication and chemical, pharmaceutical, and explosives manufacturing facilities; and to remove sulfur from process streams in petroleum refining

—Use in wire-drawing operation in the manufacture of iron and steel; as a promoter of iron catalysts in ammonia synthesis; in flotation of nonferrous ores and in the refining of ores to remove silica; and as a flux during metal refining and smelting

—Manufacture of aluminum, magnesium, calcium carbide, and sodium carbonate and in the synthesis of chemical and dye intermediates, paint pigments, pharmaceuticals, drilling fluids, and lubricants

—Use in Kraft pulp processing of paper, to clarify cane and beet sugar juices, and as a nutrient and/or dietary supplement and food additive

—Use in dehairing of hides in leather manufacture; in manufacture of pesticides, insecticides, and fungicides; and in cleaning operations as bleach, disinfectant, and deodorizer

The following methods are effective in controlling worker exposures to calcium oxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium oxide, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggra-

vated or may result in increased risk when a worker is exposed to calcium oxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with eye, skin, or respiratory system diseases.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium oxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium oxide on the eyes (especially the cornea and conjunctiva), skin, and respiratory tract. The mucosa of the nose and mouth and the nasal septum should be examined for evidence of ulceration or perforation. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium oxide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne calcium oxide is determined by using a 0.8-micron mixed cellulose ester filter (MCEF). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 400 liters is collected. The samples are ashed with nitric and hydrochloric acids. Ionization interferences are controlled with 1,000 µg/ml potassium. Analysis is conducted by atomic absorption spectroscopy with a nitrous oxide/acetylene flame. The limit of detection for this procedure is 0.03 µg/ml. This method is described in OSHA Method No. ID-121 in the *OSHA Analytical Methods Manual* [OSHA 1985]. A similar method is described in NIOSH Method 7020 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If calcium oxide contacts the skin, particles should be removed with oil or grease before they are flushed with flooding amounts of water.

Clothing contaminated with calcium oxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium oxide, particularly its potential to cause eye, skin, and upper respiratory tract irritation and burns.

A worker who handles calcium oxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium oxide or a solution containing calcium oxide is handled, processed, or stored.

STORAGE

Calcium oxide should be stored in a cool, dry, well-ventilated area in tightly sealed, airtight containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium

oxide should be protected from physical damage and should be stored separately from water and other sources of moisture, acids, oxidizers, organic materials, other combustibles, heat, and open flame. Because containers that formerly contained calcium oxide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium oxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be followed after a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of moisture.
4. Ventilate the area of the spill.
5. Do NOT use water on the spilled material; collect the spilled material and gently place it in a clean, dry container creating as little dust as possible. Cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium oxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium oxide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium oxide emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium oxide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium oxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, gauntlets, and coveralls) should be worn to prevent any skin contact with calcium oxide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to calcium oxide permeation; however, natural rubber, neoprene, and nitrile rubber have been tested against chemically similar materials (calcium hydroxide) and may provide protection for more than 8 hr. Since specific data are not available for calcium oxide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium oxide.

Goggles or face shields should be worn during operations in which calcium oxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium oxide. Contact lenses should not be worn if the potential exists for calcium oxide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM SILICATE

INTRODUCTION

This guideline summarizes pertinent information about calcium silicate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaSiO_3$

- **Synonyms**

  Calcium metasilicate, wollastonite, calcium hydrosilicate, calcium monosilicate, calcium salt of silicic acid, Calflo E, Calsil, CS Lafarge, Micro-Cel, Silene EF

- **Identifiers**

  1. CAS No.: 1344-95-2
  2. RTECS No.: VV9150000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium silicate is a noncombustible, white or cream-colored, free-flowing powder that is prepared commercially from lime and diatomaceous earth; many different calcium silicates occur in nature in mineral form (e.g., wollastonite, afwillite, grammite).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 116.16
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity (water = 1): 2.9 at 20°C (68°F)
  4. Vapor density: Data not available
  5. Melting point: 1,540°C (2,804°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water; forms a siliceous gel with mineral acids
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: None reported

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: None reported

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium silicate; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium silicate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium silicate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium silicate is 15 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable dust) for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium silicate a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on calcium silicate's local irritant properties.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium silicate can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* The toxicity of calcium silicate depends on the silica content and amount of respirable fiber in the particular calcium silicate preparation; studies in animals should be interpreted with this information in mind. Rats exposed to 10 mg/m^3 concentrations of various calcium silicate preparations, measured as respirable dust (approximately 19 to 25 mg/m^3 total dust), for 7 hr/day, 5 days/week for 224 days in a 12-month period showed no pulmonary lesions except for a few nodules in the animals exposed to the calcium silicate preparation that contained about 1% crystalline silica [ACGIH 1991]. No mesotheliomas were seen in groups of rats injected intraperitoneally with three different calcium silicate preparations [ACGIH 1991]. One experiment in rats showed a significant increase in the incidence of pleural sarcomas after wollastonite (naturally occurring calcium silicate) fibers were implanted intrapleurally [IARC 1987]. Rats, guinea pigs, and hamsters exposed for as long as 36 months to synthetic calcium silicate containing 15% asbestos at concentrations ranging from 100 to 125 million particles per cubic foot (mppcf) developed fibrosis; the authors of this study attributed the fibrosis to the asbestos in the product [ACGIH 1991].

2. *Effects on Humans:* The toxicity of calcium silicate depends on the particle size, amount of silica, the aspect ratio, and the amount of respirable fiber in the particular calcium silicate product being used; studies in humans should be interpreted with this in mind. Calcium silicate causes physical irritation when in contact with the eyes, skin, or upper respiratory tract of exposed workers. In vitro toxicity studies of calcium silicate insulation materials demonstrated equivocal hemolysis potential (one greater versus one less)

but less cytotoxicity than asbestos [ACGIH 1991]. A 23-year-old warehouse worker developed a skin reaction to calcium silicate after 3 days of exposure to an atmosphere described only as permeated with the silicate. The skin condition was characterized by patches of itchy, erythematous papular eruptions that cleared after work [Lachapelle 1984]. A study of 104 U.S. wollastonite workers with more than 1 year of exposure (mean duration of exposure approximately 9.2 years) showed no relationship between the prevalence of chronic bronchitis, airflow obstruction, or abnormal diffusing capacity in workers with increasing exposure to wollastonite [Rom 1983].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to calcium silicate include pain and redness of the eyes; itching, redness, and eruptions of the skin; and scratchiness of the throat.

2. *Chronic exposure:* Synthetic or natural materials that have calcium silicate as a base may cause dermal irritation after prolonged contact and possible induction of altered pulmonary function and lesions when silica or asbestos are also present.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium silicate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve calcium silicate and may result in worker exposures to this substance:

—Use as a substitute for materials containing silica in ceramics and as a substitute for asbestos in wallboard, insulation, and brake linings

—Use as a constituent of lime glass and Portland cement

—Use as a reinforcing filler in elastomers and plastics, paints, ceramics, paper, and wallboard

—Use as an anticaking ingredient in table salt, baking powder, foods, powdered pharmaceuticals, and cosmetics

—Use as an aggregate in road construction

—Use as a binder in refractory material, as a thermal insulator, and as a paper coating in chromatography

—Use as a veterinary antacid and absorbent

—Use as a carrier in the formulation of triazine herbicides and to provide free-flowing dust for toxic powders such as ground sulfur

The following methods are effective in controlling worker exposures to calcium silicate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium silicate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium silicate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium silicate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium silicate on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium silicate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne concentrations of calcium silicate (total dust) is determined by using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filters. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System under Dust (total) [OSHA 1989]. NIOSH has a similar method (Method 0500) that also involves gravimetric analysis [NIOSH 1984a]. The sample flow rate in the NIOSH method is between 1.5 and 2.0 liters/min. The minimum volume for an airborne concentration of 15 mg/m^3 is 15 liters, and the maximum sample volume at 15 mg/m^3 is 133 liters. The overall precision of the NIOSH method is 0.056.

A worker's exposure to airborne concentrations of calcium silicate (respirable fraction) is determined by using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is held in a 10-mm nylon cyclone, at a flow rate of 1.7 liter per minute until a maximum air volume of 800 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filters. This method has a sampling and analytical error of 0.10 and is included in the OSHA Computerized Information System under Dust (Respirable Nuisance) [OSHA 1989]. NIOSH has a similar method (Method 0600) that also involves gravimetric analysis [NIOSH 1984b]. The sample flow rate in the NIOSH method is 1.7 liter/min. The minimum volume for an airborne concentration of 5 mg/m^3 is 75 liters and the maximum sample volume at 5 mg/m^3 is 1,000 liters. The overall precision of the NIOSH method ranges from 0.043 on laboratory tests and from 0.144 to 0.227 in field tests.

PERSONAL HYGIENE

If calcium silicate contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with calcium silicate should be removed, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium silicate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cometics in areas where calcium silicate is handled, processed, or stored.

STORAGE

Calcium silicate should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of calcium silicate should be protected from physical damage. Because containers that formerly contained calcium silicate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium silicate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Use a wet method, a scoop, or a vacuum to clean up this material.
2. Place the material into a clean, dry container.
3. Cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and haz-

ardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium silicate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium silicate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium silicate emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium silicate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

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  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium silicate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with calcium silicate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions for use. No reports have been published on the resistance of various protective clothing materials to calcium

silicate permeation. If permeability data are not available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium silicate.

If calcium silicate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which calcium silicate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium silicate. Contact lenses should not be worn if the potential exists for calcium silicate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM SULFATE

INTRODUCTION

This guideline summarizes pertinent information about calcium sulfate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CaSO_4$

- **Synonyms**

  Anhydrous calcium sulfate; anhydrous gypsum; anhydrous sulfate of lime; crysalba; dead-burned gypsum; drierite; gibs; karstenite; muriacite; natural anhydrite; sulfuric acid, calcium salt; thiolite

- **Identifiers**

  1. CAS No.: 7778-18-9
  2. RTECS No.: WS6920000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Calcium sulfate is an odorless, noncombustible solid. The natural form of anhydrous calcium sulfate is known as the mineral anhydrite consisting of crystals or granules of varying color (e.g., white with a blue, gray, or reddish tinge or brick red). Insoluble anhydrite, which has the same crystal structure as the mineral, is obtained upon complete dehydration of gypsum at above 650°C. Soluble anhydrite is obtained in granular or powder form by complete dehydration of gypsum at or below 300°C in an electric oven.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 136.14
  2. Boiling point (760 mm Hg): 1,193°C (2,179.4°F)
  3. Specific gravity (water = 1): 2.96 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: 1,450°C (2,642°F)
  6. Vapor pressure at 20°C (68°F): Not applicable
  7. Solubility: Anhydrous calcium sulfate is insoluble in water but soluble in acid, ammonium salts, sodium thiosulfate, and glycerin.
  8. Evaporation rate: Not applicable

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Reactivity

1. Conditions contributing to instability: None reported

2. Incompatibilities: Explosions may result from contact of calcium sulfate with diazomethane, aluminum, or phosphorus.

3. Hazardous decomposition products: Toxic gases and particulates (such as oxides of sulfur) may be released in a fire involving calcium sulfate.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium sulfate; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Calcium sulfate will not burn. Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving calcium sulfate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium sulfate.

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for calcium sulfate is 15 mg/m^3 of air (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium sulfate (total dust) a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to calcium sulfate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to calcium sulfate can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* There is no acute information on the effects of calcium sulfate exposure in experimental animals. A month-long exposure study in animals (undefined species, route, and doses) induced bronchitis and interstitial pneumonia while exposure for 9 months caused pulmonary changes resembling those found for pneumosclerosis [Voropaev 1967]. Female rats that received four 25-mg intraperitoneal injections of calcium sulfate (gypsum) showed a slight increase in cancer rates when compared to the controls 5.7% and 0%, respectively. Mean survival rates were similar 587 days for gypsum and 592 days for controls [Pott et al. 1976].

2. *Effects on Humans:* Calcium sulfate causes irritation of the eyes, skin, mucous membranes, and upper respiratory tract in humans. Conjunctivitis, rhinitis, laryngitis, sore throat, tracheal and bronchial irritation, nosebleeds, and impaired sense of smell and taste have been reported in workers exposed to this substance [Parmeggiani 1983; Genium 1990; NLM 1991]. Although chronic lung disease has not been reported among domestic calcium sulfate workers [ACGIH 1991], a Russian paper reported that unfavorable ambient dust loads among female workers in

the gypsum industry caused increased incidences of alveolar modular fibrosis, subatrophic rhinitis, laryngitis, and pharyngitis [Voropaev 1967]. It is unclear whether the gypsum processed in Russia also contained other lung toxicants such as quartz [NLM 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to calcium sulfate can cause redness and itching of the eyes, runny nose, sore throat, and irritation of the respiratory tract and skin.

2. *Chronic exposure:* Calcium sulfate is a mucous membrane irritant that can also affect the eyes, impair the sense of smell and taste, and can cause nosebleeds. It may also cause pulmonary nodular fibrosis.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if calcium sulfate or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium sulfate and may result in worker exposures to this substance:

—Manufacture of phosphoric acid from phosphate rock

—Use as a drying agent for solids, organic liquids, and gases

—Use as a chemical intermediate in the manufacture of sulfuric acid and as a reagent in the laboratory detection of aflatoxins

—Use in the manufacture of tofu and as a dietary source of calcium in poultry

—Use as a food additive in canned vegetables, bakery products, cheeses, and as a bleaching agent in flour

—Use as an ingredient in a copper poisoning antidote in sheep

—Use as a paper filler and a component of cement

The following methods are effective in controlling worker exposures to calcium sulfate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to calcium sulfate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium sulfate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium sulfate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium silicate on the eyes, skin, and respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for calcium silicate.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history

interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

OSHA's method for the determination of worker exposure to airborne concentrations of calcium sulfate (total dust) is made by using a tared, low-ash polyvinyl chloride filter with a 5 micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Dust, Total [OSHA 1987]. NIOSH has a similar method (Method 0500), which also involves gravimetric analysis [NIOSH 1984a]. The sample flow rate in the NIOSH method is between 1.5 and 2.0 liters/min. The minimum sample volume for an airborne concentration of 15 mg/m^3 is 15 liters, and the maximum sample volume is 133 liters. The overall precision for the NIOSH method is 0.056.

OSHA's method for the determination of worker exposure to airborne concentrations of calcium sulfate (respirable fraction) is made by using a tared, low-ash polyvinyl chloride filter with a 5 micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is preceded by a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Dust (Respirable Nuisance) [OSHA 1987]. NIOSH has a similar method (Method 0600), which also involves gravimetric analysis [NIOSH 1984b]. The sample flow rate in the NIOSH method is 1.7 liter/min. The minimum sample volume for an airborne concentration of 5 mg/m^3 is 75 liters, and the maximum sample volume is 1,000 liters. The overall precision for the NIOSH method ranges from 0.043 to 0.145 in laboratory tests and from 0.144 to 0.227 in field tests.

PERSONAL HYGIENE

If calcium sulfate contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with calcium sulfate should be removed, and provisions should be made for safely removing this chemical from these articles.

A worker who handles calcium sulfate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium sulfate is handled, processed, or stored.

STORAGE

Calcium sulfate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium sulfate should be protected from physical damage and should be stored separately from aluminum, diazomethane, phosphorus, heat, sparks, and open flame. Because containers that formerly contained calcium sulfate may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving calcium sulfate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Avoid dust generation and remove all sources of heat and ignition.

2. Ventilate the area of the spill.

3. Use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Calcium sulfate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium sulfate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium sulfate emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium sulfate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium sulfate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged skin contact with calcium sulfate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to calcium sulfate permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium sulfate.

If calcium sulfate is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which calcium sulfate might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium sulfate. Contact lenses should not be worn if the potential exists for calcium sulfate exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINES FOR CHEMICAL HAZARDS

Supplement IV-OHG

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
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NOTE TO THE READER

This document is the fourth in a series of supplements to the 1981 Publication *NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards* (Washington, DC: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, DHHS [NIOSH] Publication No. 81-123). The three previous supplements are as follows:

1. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 88-118, Supplement I-OHG). This document contains 35 guidelines.

2. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 89-104, Supplement II-OHG). This document contains 30 guidelines.

3. *Occupational Safety and Health Guidelines for Chemical Hazards* (DHHS [NIOSH] Publication No. 92-110, Supplement III-OHG). This document contains 50 guidelines.

The 62 guidelines presented here in the fourth supplement include 11 revisions of previously issued guidelines and 51 new guidelines. Readers should replace the outdated guidelines in the original 1981 publication with the revised guidelines provided here.

The 62 occupational safety and health guidelines presented here are being published to disseminate technical information about chemical hazards to workers, employers, and occupational safety and health professionals. Each guideline includes (1) data on the chemical name and synoyms, cemnical and physical properties, exposure limits, and signs and symptoms of exposure, and (2) recommendations for medical monitoring, personal protective equipment, and control procedures. These recommendations reflect good industrial hygiene and medical monitoring practices, and their implementation should help employers to achieve sound occupational health programs.

The recommendations and information in these guidelines may be superseded as new information becomes available; readers should therefore regard these recommendations as general guidelines and should not rely on them for achieving compliance with occupational safety and health regulations.

The original three-volume set of guidelines and the first three supplements to the original guidelines are available through the National Technical Information Service (NTIS) (5285 Port Royal Road, Springfield, VA 22161 [telephone: 703-487-4650]). The third suuplement can also be ordered from the Superintendent of Documents (U.S. Government Printing Office, Washington, DC 20402-9325). The stock numbers for the U.S. Government Printing Office (GPO) and NTIS are as follows:

Publication	*GPO No.*	*NTIS No.*
Volumes I, II, III (DHHS [NIOSH] Publication No. 81-123)	——	PB 83-154609
Supplement I-OHG (DHHS [NIOSH] Publication No. 88-118)	——	PB 89-203129
Supplement II-OHG (DHHS [NIOSH] Publication No. 89-104)	——	PB 89-203137
Supplement III-OHG (DHHS [NIOSH] Publication No. 92-110)	017-033-00464-1	PB 93-183903

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAMPHOR, SYNTHETIC

INTRODUCTION

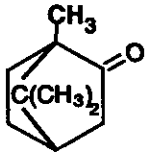
This guideline summarizes pertinent information about synthetic camphor for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_{16}O$

- **Structure**



- **Synonyms**

2-Camphanone, 2-bornanone, gum camphor, Formosa camphor, Japan camphor, matricaria camphor, 1,7,7-trimethylbicyclo(2.2.1)-2-heptanone, laurel camphor, 2-keto-1,7,7-trimethylnorcamphane

- **Identifiers**

1. CAS No.: 76-22-2
2. RTECS No.: EX1225000
3. DOT UN: 2717 32
4. DOT label: Flammable Solid

- **Appearance and odor**

Camphor is a colorless or white crystalline mass with a penetrating, aromatic odor and slightly bitter, cooling taste. The odor threshold of camphor is reported to be 0.079 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 152.23
2. Boiling point (760 mm Hg): 204°C (399.2°F) sublimes
3. Specific gravity (water = 1): 0.99 at 25°C (77°F)
4. Vapor density (air = 1 at boiling point of camphor): 5.2
5. Melting point: 179.8°C (355°F)
6. Vapor pressure at 20°C (68°F): 0.18 mm Hg

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7. Solubility: Slightly soluble in water; soluble in aniline, nitrobenzene, carbon disulfide, tetralin, decalin, methylhexalin, petroleum ether, the higher alcohols, and fixed and volatile oils. Also soluble in concentrated mineral acids in phenol, liquid ammonia, and liquid sulfur dioxide.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of camphor with strong oxidizing agents such as potassium permanganate and chromic anhydride may form explosive mixtures.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving camphor.

4. Special precautions: None

Flammability

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) for camphor.

1. Flash point: 66°C (150°F) (closed cup)

2. Autoignition temperature: 466°C (871°F)

3. Flammable limits in air (% by volume): Lower, 0.6; upper, 3.5

4. Extinguishant: Use dry chemical, sand, water spray, fog, or standard foam to fight fires involving camphor. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving camphor should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of camphor may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving camphor. Structural firefighters' protective clothing may provide limited protection against fires involving camphor.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for camphor is 2 mg/m^3 (approximately 0.3 ppm) of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for camphor of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned camphor a threshold limit value (TLV) of 2 ppm (12 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 3 ppm (19 mg/m^3) for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 min [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of irritation associated with exposure to camphor.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to camphor can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Camphor is a central nervous system toxin in animals. The toxicity can vary depending on whether the racemate or isomers were studied: *dl*, *d*, *l*, or *β* [NIOSH 1991]. The lethal concentration for mice exposed to camphor for 3 hr ranged from 400 to 1,760 mg/m^3 [Izmerov et al. 1982]. Although camphor is only slowly absorbed from subcutaneous or intramuscular injection sites, absorption from mucous membranes and alimentary tract is rapid [NLM 1991]. The lowest lethal dose by subcutaneous administration in the mouse is 2,200 mg/kg while the lowest lethal oral dose in rabbits is 2 g/kg [NIOSH 1991]. Animals acutely poisoned may exhibit mydriasis, convulsions, and central nervous system stimulation before death [NIOSH 1991]. Death by asphyxiation occurred in dogs that ingested a lethal amount (9 to 14 g) [NLM 1991]. Prolonged (duration not specified) inhalation of camphor at a concentration of 6 mg/m^3 caused injury described as severe to experimental animals; at autopsy, congestion and edema of the gastrointestinal tract, kidneys, and brain were seen [ACGIH 1991]. Subcutaneous injection of camphor in rats over an 18-month period caused no increase in the incidence of tumors, but the addition of croton oil (a known cancer promoter) to the camphor mixture caused carcinomas in 2 of 110 treated mice [ACGIH 1991].

2. *Effects on Humans:* Camphor is irritating to the nose and throat of exposed individuals; at high concentrations, it is a central nervous system stimulant and convulsant [Proctor et al. 1988]. One fatal case of camphor poisoning discussed in the literature resulted from inhalation of the vapor of heated camphor. In this case, the major symptom of overexposure was marked rigidity of the jaw muscles [ACGIH 1991]. Adults have survived ingested doses up to 1.5 grams while doses of <1 gram have been fatal. A fetal death resulted when a pregnant mother ingested camphor. Necropsy revealed severe atelectasis and central neuronal necrosis in the fetus [NLM 1991]. Serious acute overexposures to unspecified concentrations or ingested amounts can cause irritation, anxiety, headache, nausea, vomiting, excitement, restlessness, dyspnea, dizziness, confusion, delerium, hallucinations, tremors, twitching of facial muscles, spasticity, convulsions, and coma [Proctor et al. 1988; ACGIH 1991]. Death can result from respiratory failure or status epilepticus [NLM 1991]. A study of workers employed in a synthetic camphor packaging plant revealed that daily exposure (5 days/week for up to 10 months) did not cause irritation of the eyes and nose or loss of the sense of smell if the camphor concentration was maintained at or below 2 ppm [ACGIH 1991]. At this or higher concentrations, however, exposure caused eye and nose irritation and loss of the ability to smell [Proctor et al. 1988].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Camphor can cause irritation of the eyes, nose, and upper respiratory tract; anxiety; headaches; nausea; vomiting; excitement; restlessness; dyspnea; confusion; dizziness; twitching of facial muscles; spasticity; convulsions; and coma.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to camphor include irritation of the eyes and nose and loss of the sense of smell.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if camphor or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of the possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve camphor and may result in worker exposures to this substance:

—Mixing and packaging of cellulose nitrate for photographic film, cosmetics (perfumes), embalming fluid, pharmaceuticals, insect repellants, and mildew repellants

—Manufacture of plastics (especially celluloids), explosives, and incense

—Use as a plasticizer for cellulose esters and ethers, as a preservative in pharmaceuticals and cosmetics, in liniments for lumbago and related disorders, as a respiratory and circulatory stimulant, and as a topical anti-infective, counter-irritant antipruritic, and anesthetic

—Use as a catalyst or chemical intermediate in manufacturing of cumene and sulfuryl chloride, in mixing and blending of certain lacquers and varnishes, and as an odorant-flavorant during preparation and packaging of certain foods, toothpaste and powders, depilatories, deodorants. and tobacco

—Use in dentistry for the treatment of infected root canals

The following methods are effective in controlling worker exposures to camphor, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1991]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations

should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to camphor, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to camphor at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with convulsive disorders or diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to camphor exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of camphor on the central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for camphor.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne camphor is determined by using coconut shell charcoal tubes (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 25 liters is collected. The samples are desorbed with carbon disulfide methanol (99:1). Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.05 mg per sample. This method is described in NIOSH Method No. 1301, *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If camphor contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with camphor should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of camphor, particularly its potential to be an irritant of the eyes, respiratory tract, and skin.

A worker who handles camphor should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where camphor or a solution containing camphor is handled, processed, or stored.

STORAGE

Camphor should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard

[29 CFR 1910.1200]. Containers of camphor should be protected from physical damage and should be stored separately from potassium permanganate, chromic anhydride, other oxidizers, heat, sparks, and open flame. Because containers that formerly contained camphor may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving camphor, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Cover area of the spill with dry sand, vermiculite, or other noncombustible absorbent material, mix well, and place into closed containers for later disposal. Keep container tightly sealed.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) regulatory requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Camphor is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of camphor; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of camphor emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although camphor is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 CFR 355.40], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information on their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of camphor exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use

only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with camphor. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to camphor permeation, although some sources recommend the use of rubber. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to camphor.

If camphor is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which camphor might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with camphor. Contact lenses should not be worn if the potential exists for camphor exposure.

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NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

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NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPROLACTAM DUST

INTRODUCTION

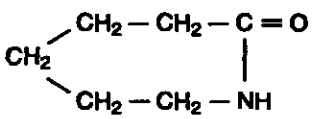
This guideline summarizes pertinent information about caprolactam dust for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NO$

- **Structure**



- **Synonyms**

Aminocaproic lactam; epsilon-caprolactam; 2-oxohexamethylenimine; 2-ketohexamethylenimine; 2-perhydroazepinone; Akulon; Alkamid; Amilan; ATM 2(Nylon); Bonamid; Capran 80; Caprolon B; Capron; Chemlon; Danamid; Durethan BK; Grilon; Itamid; Kaprolit; Maranyl; Miramid; Orgamide; Nylon X 1051; Plaskin 8200; Spencer 401; Tarlon XB; Ultramid; Vidlon

- **Identifiers (For caprolactam)**

1. CAS No.: 105-60-2
2. RTECS No.: CM3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Caprolactam dust is a white, crystalline, finely divided particulate that has an unpleasant odor.

CHEMICAL AND PHYSICAL PROPERTIES (For caprolactam)

- **Physical data**

1. Molecular weight: 113.2
2. Boiling point (760 mm Hg): 266.9°C (512.42°F)
3. Specific gravity (water = 1): 1.02 at 75°C (167°F)
4. Vapor density (air = 1 at boiling point of caprolactam dust): 3.9
5. Melting point: 70°C (158°F)
6. Vapor pressure at 20°C (68°F): 0.001 mm Hg
7. Solubility: Soluble in water, benzene, chloroform, chlorinated hydrocarbons, cyclohexene, and petroleum fractions; freely soluble in methanol, ethanol, tetrahydrofurfuryl alcohol, ether, and dimethylformamide

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8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Moisture, heat, sparks, and open flame

2. Incompatibilities: Contact of caprolactam dust with strong oxidizing agents should be avoided.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving caprolactam dust.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to caprolactam; other sources rate caprolactam's fire hazard as slight.

1. Flash point: 125°C (257°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 1.84; upper, 8.0

4. Extinguishant: Use carbon dioxide, dry chemical, alcohol foam, or water fog to fight fires involving caprolactam dust. Water or foam may cause frothing. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be used to cool fire-exposed containers.

Fires involving caprolactum dust should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving caprolactam dust.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for caprolactam dust [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 3 mg/m^3 as a STEL. A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned caprolactam dust a threshold limit value (TLV) of 1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 3 mg/m^3 for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of convulsions, dermal sensitization, and dermal and respiratory irritation [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to caprolactam dust can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, caprolactam dust is an irritant of the eyes, nose, and skin and a central nervous system depressant. Applied to the eyes of rabbits, 20 mg of this substance caused a moderate degree of irritation; 500 mg of caprolactam applied to the skin of rabbits for 24 hr caused mild skin irritation [NIOSH 1993]. The dermal LD_{50} in rabbits is 1.4 g/kg [NIOSH 1993]. Acutely poisoned animals convulsed and showed other nervous system effects before death [NIOSH 1993]. The oral LD_{50} in rats is 1.2 g/kg; the LC_{50} in the same species is 300 mg/m^3 for 2 hr [NIOSH 1993]. Administered intraperitoneally, caprolactam at doses of 350 to 600 mg/kg caused tremor, convulsions, and a bloody eye discharge [Hathaway et al. 1991]. Guinea pigs tolerated seven daily 7-hr exposures to a concentration of caprolactam ranging from 118 to 261 mg/m^3 without

evidence of adverse effects other than occasional coughing [ACGIH 1991]. Male rats exposed 4 hr/day to a 125 mg/m^3 concentration of caprolactam dust for 2.5 months showed increasing excitability, changes in spermatogenesis, and a decrease in respiratory rate and urinary function [IARC 1986]. Exposure to a 11 mg/m^3 concentration on the same regimen caused no adverse reproductive effects [IARC 1986]. In a 3-generation reproductive study in rats fed caprolactam at a dietary dose of 5,000 or 10,000 ppm, this substance caused dose-related decreases in food consumption and in body weight in dams and pups; at a dietary level of 10,000 ppm, signs of minimal kidney toxicity were seen in males at autopsy, but no reproductive or fetotoxic effects were observed [ACGIH 1991]. A 2-year carcinogenicity bioassay of caprolactam in mice and rats showed negative results [IARC 1986].

2. *Effects on Humans:* In humans, exposure to caprolactam causes eye, skin, and respiratory tract irritation, convulsions, and, in some individuals, dermal sensitization [ACGIH 1991]. Repeated exposure of the skin to the dust of caprolactam causes peeling and fissuring in chronically exposed workers [ACGIH 1991]. Workers exposed to the fumes of caprolactam (condensed from the vapor) at concentrations ranging from 6 to 131 mg/m^3 for 9 months to 13 years reported sensory irritation and dermatitis; however, no caprolactam-related pulmonary effects or signs of systemic toxicity were seen in these workers [ACGIH 1991]. Another study showed that workers repeatedly exposed to caprolactam dust (condensed vapor) generated by the spinning process complained of a bitter taste, nervousness, nose bleeds, productive cough, and dry, split mucous membranes. Some complained of flatulence, heartburn, and a heavy feeling in the stomach [ACGIH 1991]. A group of male workers exposed to several chemicals, including caprolactam dust, showed an increase in sperm abnormalities, and women occupationally exposed to this substance have been reported to have an increased rate of complications during pregnancy; however, confounding exposures and other methodological problems make interpretation of these results difficult [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to caprolactam dust may cause redness, inflammation, and tearing of the eyes; redness and inflammation of the eyelids; runny nose; scratchy throat; coughing; and redness or blistering of the skin.

2. *Chronic exposure:* Chronic exposure to caprolactam dust may cause dermatitis (fissuring, peeling, and inflammation); some individuals become sensitized to caprolactam and may have an allergic skin reaction (i.e., hives) to this substance on subsequent exposure.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if caprolactam dust or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and procedures for protecting themselves in rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve caprolactam dust and may result in worker exposures to this substance:

—Use as a chemical intermediate in the production of nylon-6 fibers and plastics

—Use as a solvent for some high molecular weight polymers

—Use in making coatings, plasticizers, paint vehicles, and synthetic leather

The following methods are effective in controlling worker exposures to caprolactam dust, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to caprolactam dust, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to caprolactam dust at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, and respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to caprolactam dust exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of caprolactam dust on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for caprolactam dust.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne caprolactam dust is determined by using an OSHA Versatile Sampler (OVS-7), 13-mm XAD-7 tube (270/140-mg sections, 20/60 mesh), with a glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 100 liters (TWA) or 15 liters (STEL) is collected. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If caprolactam dust contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with caprolactam dust should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of caprolactam dust.

A worker who handles caprolactam dust should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where caprolactam dust is present.

STORAGE

Caprolactam should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical equipment in use in storage areas should be of explosionproof design. Carrying equipment and storage containers should be grounded and bonded to prevent a dust explosion, and bulk storage systems should have an explosion-relief design. Containers of caprolactam dust should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained caprolactam dust may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving caprolactam dust, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.

5. Cover spill with sand, vermiculite, or soda ash and place material into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Caprolactam is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center about an accidental release of caprolactam dust; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of caprolactam dust emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although caprolactam dust is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of caprolactam dust exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. If the use of respirators is necessary, the only respirators permitted are those that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.1200]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with caprolactam dust. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to caprolactam dust permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to caprolactam dust.

If caprolactam dust is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which caprolactam dust might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with caprolactam dust. Contact lenses should not be worn if the potential exists for caprolactam dust exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPROLACTAM VAPOR

INTRODUCTION

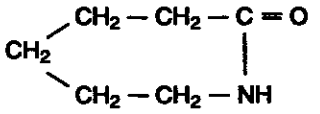
This guideline summarizes pertinent information about caprolactam vapor for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NO$

- **Structure**



- **Synonyms**

Aminocaproic lactam; epsilon-caprolactam; 2-oxohexamethylenimine; 2-ketohexamethylenimine; 2-perhydroazepinone; Akulon; Alkamid; Amilan; ATM-2 (Nylon); Bonamid; Capran 80; Caprolon B; Capron; Chemlon; Danamid; Durethan BK; Grilon; Itamid; Kaprolit; Maranyl; Miramid; Orgamide; Nylon X 1051; Plaskin 8200; Spencer 401; Tarlon XB; Ultramid; Vidlon

- **Identifiers (For caprolactam)**

1. CAS No.: 105-60-2
2. RTECS No.: CM3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Caprolactam vapor is caprolactam in the vapor state. The vapor evolves only at high temperatures, because the vapor pressure of caprolactam is low. Caprolactam vapor is colorless and has an unpleasant odor.

CHEMICAL AND PHYSICAL PROPERTIES

(For caprolactam)

- **Physical data**

1. Molecular weight: 113.2
2. Boiling point (760 mm Hg): 266.9°C (512.42°F)
3. Specific gravity (water = 1): 1.02 at 75°C (167°F)
4. Vapor density (air = 1 at boiling point of caprolactam vapor): 3.9
5. Melting point: 70°C (158°F)
6. Vapor pressure at 20°C (682°F): 0.001 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Soluble in water, benzene, chloroform, chlorinated hydrocarbons, cyclohexene, and petroleum fractions; freely soluble in methanol, ethanol, tetrahydrofurfuryl alcohol, ether, and dimethylformamide

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Moisture, heat, sparks, and open flame

2. Incompatibilities: Contact of caprolactam vapor with strong oxidizing agents should be avoided.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving caprolactam vapor.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to caprolactam vapor; other sources rate caprolactam's fire hazard as slight.

1. Flash point: 125°C (257°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 1.84; upper, 8.0

4. Extinguishant: Use carbon dioxide, dry chemical, alcohol foam, or water fog to fight fires involving caprolactam vapors. Water or foam may cause frothing. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be used to cool fire-exposed containers.

Fires involving caprolactam vapors should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving caprolactam vapor.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for caprolactam vapor [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.22 ppm (1 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.66 ppm (3 mg/m^3) as a STEL. A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned caprolactam vapor a threshold limit value (TLV) of 5 ppm (23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 10 ppm (46 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of convulsions, dermal and respiratory irritation, and dermal sensitization [NIOSH 1992]; the ACGIH limits are based on the risk of eye, skin, and upper respiratory tract irritation associated with exposure to caprolactam vapor [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to caprolactam vapor can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, caprolactam vapor is an irritant of the eyes, upper respiratory tract, and skin and a central nervous system depressant. Applied to the skin of rabbits for 24 hr, 500 mg of caprolactam caused mild skin irritation; instilled into the eyes of rabbits, 20 mg of this substance caused a moderate degree of irritation [NIOSH 1993]. The dermal LD_{50} in rabbits is 1.4 g/kg [NIOSH 1993]. Acutely poisoned animals convulsed and showed other nervous system effects before death [NIOSH

1993]. The oral LD_{50} for caprolactam in rats is 1.2 g/kg; the LC_{50} in the same species is 300 mg/m^3 for 2 hr [NIOSH 1993]. Administered intraperitoneally, caprolactam at doses of 350 to 600 mg/kg caused tremor, convulsions, and a bloody eye discharge [Hathaway et al. 1991]. Guinea pigs tolerated seven daily 7-hr exposures to a concentration of caprolactam ranging from 118 to 261 mg/m^3 without evidence of adverse effects, other than occasional coughing [ACGIH 1991]. A 2-year carcinogenicity study of caprolactam in rats and mice showed negative results [IARC 1986].

2. *Effects on Humans:* Caprolactam is a convulsant and an irritant of the eyes, nose, and throat in humans [ACGIH 1991]. Exposure to this substance has also caused skin sensitization in some individuals [ACGIH 1991]. Repeated contact of the skin with the solid causes only transient irritation, in contrast to prolonged contact with the dust, which causes dermatitis [ACGIH 1991]. At vapor concentrations that occasionally peaked at 100 ppm (460 mg/m^3), polymer plant workers reported experiencing severe and dose-related eye, nose, and throat irritation; eye irritation was not experienced below a concentration of 25 ppm, but transient nose and throat irritation occurred in some workers even at vapor concentrations of 10 ppm (46 mg/m^3) [ACGIH 1991]. Volunteers exposed to caprolactam vapor for unspecified periods at concentrations ranging from 53 to 521 mg/m^3 reported eye and upper respiratory tract irritation [ACGIH 1991]. A group of male workers exposed to caprolactam and other chemicals showed an increase in sperm abnormalities, and women occupationally exposed to this substance are reported to have experienced an increased rate of complications during pregnancy; however, confounding exposures and other methodological problems make interpretation of these results difficult [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to caprolactam vapor may cause redness, inflammation, and burning of the eyes; runny nose; scratchy throat; productive cough; transient skin redness; nose bleeds; a bitter taste in the mouth; and a feeling of nervousness.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to caprolactam vapor have been reported.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during an emergency.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve caprolactam vapor and may result in worker exposures to this substance:

—Use as a chemical intermediate in the production of nylon-6 fibers and plastics

—Use as a solvent for some high molecular weight polymers

—Use in making coatings, plasticizers, paint vehicles, and synthetic leather

The following methods are effective in controlling worker exposures to caprolactam vapor, depending on the feasibility of implementation:

—Process enclosure

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- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to caprolactam vapor, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to caprolactam vapor at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to caprolactam vapor exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of caprolactam vapor on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individ-

ual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for caprolactam vapor.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne caprolactam vapor is determined by using an OSHA Versatile Sampler (OVS7), 13-mm XAD-7 tube (270/140-mg sections, 20/60 mesh), with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 100 liters (TWA) or 15 liters (STEL) is collected. Analysis is conducted by high-performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If caprolactam vapor contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with caprolactam vapor should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laudering contaminated clothing should be informed of the hazardous properties of caprolactam vapor.

A worker who is exposed to caprolactam vapor should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where caprolactam vapor is present.

STORAGE

Caprolactam should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All electrical equipment in use in storage areas should be of explosionproof design. Containers of caprolactam vapor should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained caprolactam vapor may still hold product residues, they should be handled appropriately.

LEAKS

In the event of a leak involving caprolactam vapor, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Do not touch the leaked material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Cover the leaked material with sand, vermiculite, or soda ash and place material into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Caprolactam vapor is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release

notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of caprolactam vapor; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of caprolactam vapor emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although caprolactam vapor is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of caprolactam vapor exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with caprolactam vapor. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to caprolactam vapor permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to caprolactam vapor.

Safety glasses, goggles, or face shields should be worn during operations in which caprolactam vapor might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with caprolactam vapor. Contact lenses should not be worn if the potential exists for caprolactam vapor exposure.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPTAFOL

INTRODUCTION

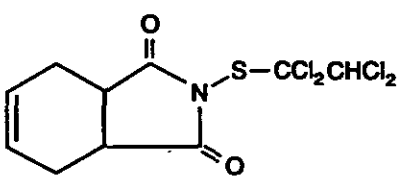
This guideline summarizes pertinent information about captafol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_9Cl_4NO_2S$

- **Structure**



- **Synonyms**

Difolatan; Captofol; Sanspor; Sulfonimide; 3a,4,7,7a-tetrahydro-2-((1,1,2,2-tetrachloroethyl)thio)-1-H-isoindole-1,3(2H)-dione; Alfloc 7020; Difosan; Folcid; Haipen 50; N-((1,1,2,2-tetrachloroethyl)sulfenyl)-cis-4-cyclohexene-1,2-dicarboximide; Nalco 7046; Ortho 5865; Proxel EF; cis-N-((1,1,2,2-tetrachloroethyl)thio)-4-cyclo-hexene-1,2-dicarboximide

- **Identifiers**

1. CAS No.: 2425-06-1
2. RTECS No.: GW4900000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Captafol is a noncombustible, white, crystalline substance with a characteristic odor. It is available commercially in the form of a liquid or wettable powder.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 349.06
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): Data not available
4. Vapor density: Not applicable
5. Melting point: 160° to 161°C (320° to 321.8°F) (decomposes)
6. Vapor pressure at 20°C (68°F): Data not available
7. Solubility: Insoluble in water; slightly soluble in acetone and most organic solvents; freely soluble in toluene.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Strongly alkaline conditions

2. Incompatibilities: Contact of captafol with acids or acid vapors may cause violent reactions.

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen and sulfur) may be released in a fire involving captafol.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to captafol; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving captafol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving captafol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for captafol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure. However, captafol has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned captafol a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek with a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the sensitization effects associated with exposure to captafol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to captafol can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Captafol is a liver and kidney toxicant; it also has fetotoxic and teratogenic effects in experimental animals. When instilled into rabbits' eyes it caused irritation of the conjunctiva and iris that lasted 21 days [ACGIH 1991]. Moderate skin irritation resulted when rabbits were dermally exposed to captafol for 72 hr [ACGIH 1991]. The dermal LD_{50} in the rabbit is 9 g/kg while it is <15 g/kg for the 80% wettable powder [NLM 1991; ACGIH 1991]. Rat oral LD_{50}s range from 2.5 to 6.8 g/kg [ACGIH 1991]. Dogs given 100 or 300 mg/kg captafol (route not specified) in a 2-yr study developed mild anemia and showed growth deficiency; the livers and kidneys of these animals and those given 30 mg/kg were slightly enlarged but showed no functional abnormalities [Hayes 1982]. Captafol is fetotoxic and/or teratogenic in rats, rabbits, and hamsters by the oral or peritoneal routes of exposure [NIOSH 1991; NLM 1991]. Captafol is also an experimental mutagen: it was positive in one in vivo and several in vitro tests [NLM 1991]. In a 2-yr cancer bioassay, rats were fed captafol at dietary levels of 250, 500,

1,500, or 5,000 ppm. Animals in the two highest dose groups did not grow normally and had enlarged livers; mortality was increased in animals dosed at the highest level. On microscopic examination, the livers and kidneys of animals given 1,500 or 5,000 ppm captafol showed kidney and pronounced degenerative liver changes, although there was no evidence of tumors [Hayes 1982; Clayton and Clayton 1981]. A second chronic study has confirmed captafol to be a carcinogen in treated mice [ACGIH 1991].

2. *Effects on Humans:* In humans, captafol is an irritant and sensitizer of the skin and upper respiratory system. Reactions to acute overexposure to captafol may be severe; sensitized workers develop wheezing and bronchitis [Clayton and Clayton 1981]. A 1969 survey of Japanese farmers reported a 25% incidence of occupational dermatitis in these workers; those farmers who had developed acute contact dermatitis had been engaged in the application of captafol and had developed red and swollen eyelids and dermatitis that was aggravated by light (phototoxic dermatitis). The skin eruptions typically appeared 1 to 3 days after contact and usually disappeared within a week after the cessation of exposure [Hayes 1982]. In one study, 23% of agricultural workers exposed to captafol reported episodes that suggested occupationally induced dermatitis [NLM 1991]. Another study reports that many of the captafol-exposed workers who had developed skin rash also showed signs of systemic toxicity: hypertension, anemia, decreased liver function, decreased excretion of urinary protein and urobilinogen, and depressed cholinesterase activity [Hayes 1982; ACGIH 1991]. Ingestion of large quantities have caused vomiting and diarrhea [NLM 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Captafol can induce wheezing, bronchitis, coughing, redness and tearing of the eyes, red and swollen eyelids, and reddened and blistered skin.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to captafol may include raised, itching, reddened, and blistered eruptions of the skin, asthmatic wheezing, hypertension, anemia, and decreased red blood cell cholinesterase activity and elevated liver function.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if captafol or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** use syrup of ipecac if large amounts of captafol are ingested.

—Do *not* induce vomiting if captafol has been mixed with a petroleum distillate such as kerosene or diesel fuel.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve captafol and may result in worker exposures to this substance:

—Manufacture of captafol or captafol mixtures

—Formulation of captafol-containing fungicides

—Application of captafol-containing fungicides to tomatoes, potatoes, coffee plants, logs, and wood products

The following methods are effective in controlling worker exposures to captafol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to captafol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to captafol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of

exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory system and skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to captafol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of captafol on the respiratory system and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for captafol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne captafol is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm tube (270/140 mg sections, 20/60 mesh) that has a glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 240 liters is collected. Analysis is conducted by gas chromatography using an electron capture detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989]

PERSONAL HYGIENE

If captafol contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with captafol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of captafol, particularly its potential to cause skin sensitization.

A worker who handles captafol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where captafol or a solution containing captafol is handled, processed, or stored.

STORAGE

Captafol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of captafol should be protected from physical damage and should be stored separately from acids, acid fumes, strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained captafol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving captafol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small dry spills, collect material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in an approved facility.

6. If captafol is in liquid or slurry form, absorb it with vermiculite, dry sand, earth, or a similar method.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Captafol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of captafol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of the SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of captafol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although captafol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with captafol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to captafol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to captafol.

If captafol is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which captafol might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with captafol.

REFERENCES CITED

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CAPTAN

INTRODUCTION

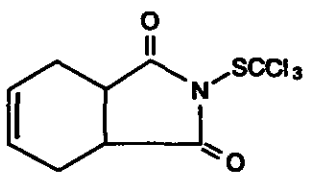
This guideline summarizes pertinent information about captan for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_8Cl_3NO_2S$

- **Structure**



- **Synonyms**

N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide; 3a,4,7,7a-tetrahydro-2-[(trichloromethyl)thio]-1H-isoindole-1,3(2H)-dione; AA Captan; Agrosol S; Agrox 2-Way and 3-Way; Amercide; Bangton; Bean Seed Protectant; Captaf; Captex; Esso Fungicide 406; Flit 406; Glyodex 37-22; Hexacap; Isotox Seed Treater "D" and "F"; Kaptan; Malipur; Merpan; Neracid; Orthocide; Vancide P-75; Vanicide

- **Identifiers**

1. CAS No.: 133-06-2
2. RTECS No.: GW5075000
3. DOT UN: 9099 31
4. DOT label: None

- **Appearance and odor**

Captan is an odorless, white, crystalline solid that can also be found as a yellow powder. This substance is available as a powder or in a variety of liquid formulations.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 300.57
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.74 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 178°C (352.4°F) (decomposes)

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6 Vapor pressure at 25°C (77°F): Less than 0.00001 mm Hg

7. Solubility: Practically insoluble in water; soluble in acetone, benzene, chloroform, cyclohexanone, isopropanol, and xylene; insoluble in petroleum oils.

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Heat and alkalinity

2. Incompatibilities: Tetraethyl pyrophosphate and emulsifiable concentrate formulations of parathion

3. Hazardous decomposition products: Toxic gases (such as chlorine, phosgene, and oxides of nitrogen and sulfur) may be released in a fire involving captan.

4. Special precautions: Captan cannot be used with strong alkalies or with oil sprays.

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to captan; this substance may burn, but it does not ignite readily.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or alcohol foam.

Fires involving captan should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of captan may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving captan. Structural firefighters' protective clothing may provide limited protection against fires involving captan.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for captan [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. However, captan has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned captan a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer that is associated with exposure to captan [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to captan can occur through inhalation, ingestion, and eye and skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, captan is an irritant and sensitizer of the skin. When applied to the skin of experimental animals (species not identified) at a dose of 900 mg/kg, captan caused slight irritation [ACGIH 1991], while previously exposed guinea pigs developed a moderate degree of sensitization when rechallenged [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is greater than 9 g/kg [Clayton and Clayton 1981]. The 2-hr LC_{50}s for male and female mice are 4,500 and 5,000 mg captan/m^3, respectively [ACGIH 1991]. However, mechanical

milling of that technical material reduced the 2-hr LC_{50}s in mice to 1,700 and 3,700 mg/m^3, respectively. Estimated inhalation absorption levels for the milled material were calculated to be 142 mg/kg for the males and 310 mg/kg for the females. The 2-hr LC_{50} for rats is greater than 5,700 mg/m^3 for unmilled captan [Stevens et al. 1978]. The lowest reported oral LD50s in mice and rats are 7,500 and 8,400 mg/kg [ACGIH 1991; IARC 1983]. Laboratory animals given very high doses (not further specified) of captan became hypothermic, irritable, anorectic, and listless; they also had hyporeflexia and oliguria [EPA 1989]. When tested in mice, rats, dogs, and monkeys at doses below those that are maternally toxic, captan failed to produce teratogenic effects by the oral, subcutaneous, or inhalation route of administration [Hayes 1982]. Although captan has not been shown to be teratogenic, feeding at maternally toxic doses has caused fetotoxicity (increased resorptions and decreased fetal weights) and possible terata (e.g., shortened forelimbs, cleft palate, fused ribs, exencephaly) among the offspring of some species [NLM 1991; IARC 1983]. Feeding studies demonstrated no effects in dogs fed 100 mg/kg/day for 66 weeks, but feeding at a dose of 300 mg/kg/day caused a slight increase in liver and kidney weights [Hayes 1982; ACGIH 1991]. Female rats fed 1,000 or 5,000 ppm captan in their diet (about 250 mg/kg/day) for 2 yr showed growth retardation; at twice this dose, captan caused growth depression in animals of both sexes and testicular atrophy in the males [Clayton and Clayton 1981; Hayes 1982]. Captan is mutagenic in direct contact with susceptible cells, but it is not mutagenic in intact animals, except perhaps at very high doses [Hayes 1982]. Captan was tested for carcinogenicity in mice and rats by dietary administration; it was carcinogenic in one strain of mice, in which it caused a statistically significant increase in the incidence of duodenal tumors [IARC 1983]. The International Agency for Research on Cancer (IARC) has concluded that there is limited evidence that captan is carcinogenic in experimental animals [IARC 1983]. Subsequent to the IARC review, rats and mice that were administered captan in their diets for 80 weeks developed neoplasms, including cancers. Rats developed neoplasms of the ovary, liver, and the pituitary, adrenal, and mammary glands. Mice had increased numbers of duodenal neoplasms [NLM 1991].

2. *Effects on Humans:* In humans, captan is an irritant of the eyes, skin, and upper respiratory tract and a skin sensitizer [Hayes 1982; Klaassen et al. 1986; Clayton and Clayton 1981]. Skin contact with captan has caused severe sensitivity in some workers, and an estimated 3% to 5% of the exposed population could become sensitized [IARC 1983]. An 18-year-old gardener was confirmed as having recurrent urticaria from exposure to captan [NLM 1991]. A 1,071 mg/kg dose of captan caused the death of one individual [NIOSH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Captan can induce redness, pain, and tearing of the eyes; runny nose; scratchy throat; difficult breathing; and redness, itching, and cracking of the skin.

2. *Chronic exposure:* Captan-sensitized workers can develop redness, raised areas, blistering, and itching of the skin.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if captan or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve captan and may result in worker exposures to this substance:

—Manufacture and formulation of captan-containing fungicides and bactericides

—Use as a fungicide to control scab, black root, botrytis, sooty blotch, and summer rots on apples and for control of a wide variety of fungal diseases on small fruits, berries, vegetables, and ornamental crops

—Use as a bacteriostat in soaps

—Use as a fungicide in paints, lacquers, paper, rubber stabilizers, vinyl resins, plastics, leather fabrics, and to preserve cosmetics and fruits

—Use as a bacteriostat and fungicide in veterinary medicine

The following methods are effective in controlling worker exposures to captan, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to captan, a licensed health care professional should evaluate and document the worker's baseline

health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to captan at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory tract or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to captan exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of captan on the respiratory tract or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for captan.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne captan is determined by using an OSHA Versatile Sample (OVS-2) with a 13-mm XAD-2 tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 60 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

If captan contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with captan should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of captan, particularly its potential to cause skin sensitization.

A worker who handles captan should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where captan or a solution containing captan is handled, processed, or stored.

STORAGE

Captan should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of captan should be protected from physical damage and should be stored separately from water and heat. Because containers that formerly contained captan may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving captan, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the captan for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Captan is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for captan is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of captan per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of captan emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although captan is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this

substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of captan exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with captan. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to captan permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to captan.

If captan is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which captan might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with captan. Contact lenses should not be worn if the potential exists for captan exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBARYL

INTRODUCTION

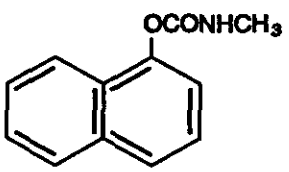
This guideline summarizes pertinent information about carbaryl for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{11}NO_2$

- **Structure**



- **Synonyms**

Sevin, 1-naphthyl n-methylcarbamate, alpha-naphthyl n-methylcarbamate, methylcarbamic acid-1-naphthyl ester

- **Identifiers**

1. CAS No.: 63-25-2
2. RTECS No.: FC5950000
3. DOT UN: 2757 55
4. DOT label: None

- **Appearance and odor**

Carbaryl is an odorless white, gray, or colorless solid. This substance is a carbamate pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 201.22
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.23 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 142°C (287.6°F)
6. Vapor pressure at 25°C (77°F): <0.00004 mm Hg
7. Solubility: Nearly insoluble in water; moderately soluble in dimethylformamide, acetone, isophorone, and cyclohexanone.
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: Unstable above 70°C (148°F); hydrolyzes in alkalies

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2. Incompatibilities: Contact of carbaryl with strong oxidizers may cause fires and explosions. Carbaryl is also incompatible with strongly alkaline pesticides.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, methylamine, and carbon monoxide) may be released in a fire involving carbaryl.

4. Special precautions: None

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to carbaryl. This substance is not flammable, although other constituents of carbaryl formulations may be flammable or combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinquishant that is suitable for the materials involved in the surrounding fire.

Fires involving carbaryl should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbaryl formulations may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbaryl. Chemical protective clothing that is specifically recommended for carbaryl may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving carbaryl.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbaryl is 5 mg/m^3 as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for carbaryl is 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbaryl a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of teratogenic, systemic, and other effects associated with exposure to carbaryl, and the NIOSH limit is based on the risk of central nervous system and reproductive effects associated with exposure to carbaryl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbaryl can occur through inhalation, eye and skin contact, percutaneous absorption, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* Carbaryl inhibits cholinesterase enzyme activity in the central, autonomic, and peripheral nervous systems. This chemical was mildly irritating to exposed rabbit eyes and severely irritating to rabbit skin following a 24-hr contact period [NIOSH 1992b]. Guinea pigs showed a weak skin sensitization reaction to carbaryl [Carpenter et al. 1961]. The dermal LD_{50} is 4,000 mg/kg for rats and 2,000 mg/kg for rabbits [NIOSH 1992b]. Goats acutely drenched with carbaryl developed anorexia, diarrhea, dullness, weakness, frothing, nasal discharge, recumbency, and death. Histopathology of necropsied tissues revealed hyperemia of the CNS, heart, liver, and kidney plus myocardial and neuronal degeneration [NLM 1992]. The lowest reported oral LD_{50} for mice is 128 mg/kg, and for rats it is 230 mg/kg [NIOSH 1992b]. Dogs were given a single

oral dose of carbaryl (250, 375, or 500 mg/kg); animals in the two higher dose groups showed signs of nervous system stimulation: lacrimation, excessive salivation, muscular twitching, incoordination, vomiting, defecation, and urination [Carpenter et al. 1961]. In the dogs given 375 mg/kg carbaryl, red blood cell cholinesterase activity was depressed by 24% to 33% [Carpenter et al. 1961]. Rats that received doses ranging from 7 to 70 mg/kg for up to 12 months developed marked functional and structural changes of the pituitary gland plus impairment of thyroid and gonadal function [IARC 1976]. Long-term exposure of pigs resulted in the induction of a progressive structural neuromyopathy that was not acutely reversible with atropine [NIOSH 1992b]. Male rats exposed to 200 mg/kg three times a week for 13 weeks did not develop adverse reproductive effects, but doses of 70 mg/kg (dosing schedule undefined) for 1 year caused reduced sperm motility and alterations in spermatogenesis [NIOSH 1992b]. Female rats exposed to a total dose of 1,370 mg/kg over 39 weeks developed menstrual cycle changes, and exposure of other rats to 5,475 mg/kg over 52 weeks caused uterine, cervix, vaginal, ovarian, and fallopian tube alterations [NIOSH 1992b]. Carbaryl has not been shown to be teratogenic at doses below those causing maternal toxicity [Proctor et al. 1988]. Carbaryl is a mutagen in a wide variety of in vitro and in vivo tests [NIOSH 1992b]. Based on a review of the results of carcinogenicity bioassays in mice and rats, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of this substance in animals is inadequate [IARC 1987].

2. *Effects on Humans:* Carbaryl causes reversible cholinesterase inhibition in humans; this effect causes acetylcholine to accumulate at synapses in the nervous system, at neuromuscular junctions of the skeletal and smooth muscles, and in the secretory glands. In two separate incidents, a liquid insecticide (carbaryl/dimethoate mixture) was splashed into a person's eyes, causing transient injury to the corneal epithelium and swelling of the lids [NIOSH 1992b]. Dermal application of carbaryl to the forearm resulted in urinary excretion of 74% of the dose applied [IARC 1976]. A single oral dose of 250 mg carbaryl (approximately 2.8 mg/kg) caused the sudden onset of abdominal pain followed by profuse sweating, lethargy, and vomiting in an adult man; after treatment, this individual recovered completely. An individual who had consumed 21 g of carbaryl (500 mg/kg) recovered from acute cholinesterase inhibition but suffered weakness of the arms and legs and had electrophysiologic findings consistent with a diagnosis of peripheral neuropathy [NIOSH 1992b]. A 75-year-old man who had excessive long-term exposure to carbaryl recovered from cholinesterase inhibition when removed from exposure, but sleep apnea and peripheral neuropathy appeared as late clinical features [NIOSH 1992b]. A group of 59 workers exposed for 19 months to carbaryl concentrations ranging from 0.23 to 31 mg/m^3 showed no overt signs or symptoms of carbamate poisoning, although their red blood cell cholinesterase activity was slightly depressed [Proctor et al. 1988]. Testicular dysfunction and abnormalities in the shape of sperm have been reported in carbaryl-exposed workers [Schrag and Dixon 1985; Wyrobek et al. 1980, 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbaryl-induced chloinesterase inhibition can cause nausea, vomiting, abdominal cramps, and diarrhea; excessive sweating and salivation; lethargy and weakness; runny nose and a sensation of tightness in the chest; contracted pupils, blurred vision, tearing, and pain in the eyes; loss of coordination, tremors, and slurring of speech; increasingly difficult respiration, convulsions, and coma. If the poisoning is severe, death from respiratory failure may follow.

2. *Chronic exposure:* Carbaryl has induced headache, memory loss, anorexia, weight loss, proximal muscle weakness, fasciculations, cramps, sleep apnea, and peripheral neuropathy.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbaryl or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** induce vomiting if carbaryl has been mixed with a petroleum distillate such as kerosene or diesel fuel.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The use of carbaryl as a molluscicide, acaricide, and insecticide (for fruits, vegetables, cotton, tobacco, ornamental trees, livestock, poultry, and pets) may result in worker exposure to this chemical.

The following methods are effective in controlling worker exposures to carbaryl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) period-

ically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to carbaryl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the red blood cell cholinesterase activity.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbaryl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with cholinesterase inhibition.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbaryl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbaryl on red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. A pre-exposure blood cholinesterase concentration should be obtained for each worker so that the postexposure concentration may be expressed as a percentage of that subject's normal cholinesterase activity. A postexposure blood cholinesterase concentration that is less than 70% of normal is considered indicative of excessive exposure to carbaryl. Although the relationship between airborne concentrations of carbaryl and urinary concentrations of 1-naphthal has not been established, urinary concentrations of 1-naphthal in excess of 4 mg/liter urine may reflect overexposure to carbaryl.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbaryl is determined by an OSHA versatile sampler (OVS-2) containing two sections of XAD-2 resin (270/140-mg sections, 20/60 mesh) and a glass fiber filter. Sampling tubes can be obtained from OSHA's Salt Lake City Analytical Laboratory. Samples are collected at a maximum flow rate of 1 liter/min until a maximum air volume of 60 liters is collected. The samples are extracted with acetonitrile. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. The limit of detection for this procedure is 0.08 mg/m^3. This method is described in Method No. 63, OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If carbaryl contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min and then wash with soap and water.

Clothing contaminated with carbaryl should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbaryl, particularly its potential to cause cholinesterase inhibition.

A worker who handles carbaryl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbaryl or a solution containing carbaryl is handled, processed, or stored.

STORAGE

Carbaryl should be stored in a cool, dry, continuously ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbaryl should be protected from physical damage and should be stored separately from strong oxidizers, strongly alkaline pesticides, heat, sparks, and open flame. Because containers that formerly contained carbaryl may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbaryl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
5. Absorb small liquid spills with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the carbaryl for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbaryl is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbaryl is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of carbaryl per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbaryl emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity,

reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbaryl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbaryl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, full-body coveralls, and impervious footwear) should be worn to prevent repeated or prolonged skin contact with carbaryl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by carbaryl and may provide protection for more than 4 but fewer than 8 hr: natural rubber, neoprene, nitrile rubber, and polyvinyl chloride.

If carbaryl is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbaryl might contact the eyes (e.g., through splashes of carbaryl-containing formulations). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbaryl. Contact lenses should not be worn if the potential exists for carbaryl exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBOFURAN

INTRODUCTION

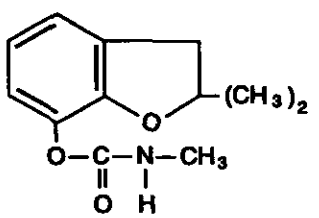
This guideline summarizes pertinent information about carbofuran for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{15}NO_3$

- **Structure**



- **Synonyms**

Bay 70143; Niagra 10242; Furadan; Furodan; Yaltox; Curaterr; Chinufur; 2,2-dimethyl-2,2-dihydrobenzofuranyl-7-N-methylcarbamate; methyl carbamic acid 2,3-dihydro-2,2-dimethyl-7-benzofuranyl ester

- **Identifiers**

1. CAS No.: 1563-66-2
2. RTECS No.: FB9450000
3. DOT UN: 2757 55
4. DOT label: Poison B

- **Appearance and odor**

Carbofuran is a noncombustible, odorless, colorless or white crystalline solid available commercially in the form of wettable powder, granules, or flowable paste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 221.26
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.18 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of carbofuran): Data not available
5. Melting point: 150° to 152°C (302° to 305.6°F)
6. Vapor pressure at 33°C (91.4°F): 0.00002 mm Hg
7. Solubility: Slightly soluble in water; soluble in ace-

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

tone, acetonitrile, benzene, cyclohexanone, and other organic solvents. In the conventional solvent formulations used in agriculture, carbofuran is essentially insoluble.

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Heat, sparks, flame, or contact with an alkaline substance

2. Incompatibilities: Fires and explosions may result from contact of carbofuran with alkaline media, acids, or strong oxidizers (such as perchlorates, peroxides, chlorates, nitrates, and permanganates).

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving carbofuran.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to carbofuran; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving carbofuran.

Fires involving carbofuran should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbofuran may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbofuran. Chemical protective clothing that is specifically recommended for carbofuran may provide little or no thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving carbofuran.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for carbofuran [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbofuran a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to carbofuran.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbofuran can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbofuran is a potent but reversible cholinesterase inhibitor. Instillation of carbofuran into the conjunctival sac caused miosis and paralysis of the ciliary muscle, both reversed by installation of atropine [Tobin 1970]. There are widely divergent dermal LD_{50}s for rabbits which range from 885 mg/kg [NIOSH 1992b] to 10,200 mg (98% carbofuran)/kg [Tobin 1970]. The rat dermal LD_{50} is 120 mg/kg [NIOSH 1992b]. The LC_{50} in rats is 85

mg/m^3 for an unspecified period [NIOSH 1992b]. Monkeys which inhaled a 75% wettable powder (wp) dust for 6 hr at an airborne concentration of 0.86 mg/m^3 showed slight but significant cholinesterase inhibition; at an exposure of 0.56 mg/m^3 for the same period, no effects were seen. In addition, a monkey had sporadic tremors following a 30-min exposure to 1.3 mg/m^3. Another exposed to 1.8 mg/m^3 for 260 min developed only emesis [Tobin 1970]. The oral LD_{50}s for mice, rats, and dogs are 2, 5, and 19 mg/kg, respectively [NIOSH 1992b]. In experimental animals given high but non-lethal doses of carbofuran, normal cholinesterase activity returned within 6 hr [NLM 1991]. Dogs fed 50 ppm carbofuran in a chronic feeding study (length of study not specified) showed significant inhibition of plasma, erythrocyte, and brain cholinesterase levels; the no-effect levels in dogs and rats were 20 ppm (dogs) and 25 ppm (rats) [ACGIH 1991]. Administered to rats by gavage on day 18 of gestation, a dose of 2.5 mg/kg carbofuran produced cholinergic signs within 5 minutes and killed 25% of the dams within 30 minutes; a dose of 0.05 mg/kg produced nervous system effects in the dams but not in the fetuses [Hayes 1982]. No adverse reproductive or developmental effects were induced in three successive generations of rats which consumed diet containing carbofuran (10 mg/kg diet) or in dogs on a 50 mg carbofuran/kg diet for one generation [NIOSH 1992b]. When mice, rats, rabbits, and dogs consumed diets containing carbofuran (100 mg/kg), the only effect induced was decreased survival rates in rat pups [Shepard 1986]. Carbofuran is mutagenic in bacterial and mammalian test systems [NIOSH 1992b; NLM 1991].

2. *Effects on Humans:* In humans, carbofuran is a rapidly reversible cholinesterase inhibitor. No effects have been reported in workers exposed to carbofuran concentrations approaching 0.1 mg/m^3 per day [NLM 1991]. Several cases of carbofuran poisoning have been reported in laboratory and pilot plant personnel and applicators. These workers developed weakness, malaise, profuse perspiration, lightheadedness, paleness, nausea, blurred vision, loss of depth perception, hypersalivation, poor coordination, and vomiting. Recovery took up to 4 hr in the absence of atropine treatment and less than 30 min when it was administered. No systemic toxicity was observed when only ocular effects were induced [Tobin 1970]. Seventy-four of 142 teenage workers who worked in a field that had been sprayed with carbofuran the previous day experienced pronounced symptoms of nervous system poisoning, including dizziness, nausea, and/or blurred vision; however, all of these workers responded quickly and completely to therapy [Hayes 1982]. Carbofuran is mutagenic in human lymphocyte cells [NIOSH 1992b].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbofuran can cause muscle weakness, dizziness, profuse sweating, headache, salivation, nausea, vomiting, abdominal pain, diarrhea, contracted pupils, incoordination, slurred speech, difficult breathing, chest tightness, blurred vision, muscle twitching and spasms. Convulsions may occur.

2. *Chronic exposure:* Based on effects seen in animals, long-term exposure to low levels of carbofuran is likely to cause cholinesterase inhibition.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Carbofuran can be absorbed through the skin in lethal amounts. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbofuran or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do ***not*** induce vomiting if carbofuran has been mixed with a petroleum distillate such as kerosene or diesel fuel.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbofuran and may result in worker exposures to this substance:

—Use as an acaricide, miticide, nematocide, and insecticide

—Manufacture of carbofuran

—Formulation of carbofuran for use as a pesticide

The following methods are effective in controlling worker exposures to carbofuran, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to carbofuran, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate

on the function and integrity of the blood and on the individual's pre-exposure plasma and red blood cell cholinesterase activity levels.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbofuran at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reduced plasma or red blood cell cholinesterase activity levels.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbofuran exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbofuran on plasma or red blood cell cholinesterase activity levels. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of overexposure to organophosphorus compounds such as carbofuran. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for carbofuran (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability. Absorption of carbofuran can be confirmed by analysis of urine for its metabolite, carbofuran phenol. However, correlations between airborne and urinary levels of carbofuran and its metabolite have not been established.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbofuran is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140-mg sections, 20/60 mesh). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 480 liters is collected. The sample is then treated with acetonitrile to extract the carbofuran. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If carbofuran contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with carbofuran should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbofuran.

A worker who handles carbofuran should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbofuran or a solution containing carbofuran is handled, processed, or stored.

STORAGE

Carbofuran should be stored in a cool, dry, continuously-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbofuran should be protected from physical damage and should be stored separately from acids, strong oxidizers (such as perchlorates, peroxides, and nitrates), heat, sparks, and open flame. Because containers that formerly contained carbofuran may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbofuran, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.

4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

5. For liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 10,000 lb or more of carbofuran must comply with EPA's emergency planning requirements. (If carbofuran is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 10 lb or more of carbofuran are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for carbofuran is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbofuran emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbofuran is not specifically listed as

a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbofuran exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with carbofuran. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to carbofuran permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to carbofuran.

If carbofuran is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbofuran might contact the eyes (e.g., through dust particles or splashes of carbofuran-containing solutions). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbofuran. Contact lenses should not be worn if the potential exists for carbofuran exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBON BLACK

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about carbon black and carbon black containing polycyclic aromatic hydrocarbons (PAH's) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Synonyms:** Channel black, furnace black, thermal black
- **Identifiers:** CAS 1333-86-4; RTECS FF5800000; DOT Not assigned
- **Appearance and odor:** Odorless black solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Specific gravity (water = 1): 1.8 to 2.18
2. Vapor pressure at 20°C (68°F): Essentially zero
3. Insoluble in water

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers (e.g., chlorates, bromates, and nitrates) may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving carbon black.
3. Caution: Carbon black dust may form explosive mixtures in air.

- **Flammability**

1. Minimum dust ignition temperature: 510°C (950°F)
2. Extinguishant: Water or carbon dioxide
3. Combustible solid, (NFPA)

- **Warning properties**

1. Evaluation of warning properties for respirator selection (carbon black): Based on lack of information on irritation levels, carbon black should be considered to have poor warning properties.
2. Evaluation of warning properties for respirator selection (carbon black containing PAH's): Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbon black is 3.5 milligrams of carbon black per cubic meter of air (mg/m^3) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for carbon black is 3.5 mg/m^3 as a TWA for up to a 10-hour workshift, 40-hour workweek. NIOSH recommends that carbon black containing PAH's at a concentration greater than 0.1% be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH REL for PAH's that may be formed during the manufacture of carbon black and that could be adsorbed on the carbon black is 0.1 mg/m^3 (measured as the cyclohexane-extractable fraction) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 3.5 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for carbon black

	Exposure limits mg/m^3
OSHA PEL TWA	3.5
NIOSH REL TWA (carbon black)	3.5
TWA (PAH's) (Ca)*	0.1
ACGIH TLV® TWA	3.5

* (Ca): NIOSH recommends treating as a potential human carcinogen when the concentration of PAH's is greater than 0.1%.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon black may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

• **Summary of toxicology**

1. *Effects on animals:* Inhalation of carbon black by mice, rats, and monkeys caused thickened alveolar walls, increased pulmonary collagen, right atrial and ventricular strain, hypertrophy of the right and left ventricles and septum, and increased heart weights. Although carbon black itself did not cause cancer in treated animals, carbon black containing polynuclear hydrocarbons (PNA's) or PAH's did cause cancer following chronic administration by all routes tested.

2. *Effects on humans:* Chronic inhalation exposure of production workers has caused decreased pulmonary function and myocardial dystrophy. There is suggestive but inconclusive evidence that carbon black containing PAH's has been responsible for induction of skin cancer in exposed workers.

• **Signs and symptoms of exposure**

Long-term (chronic): Inhalation of carbon black can cause cough, phlegm, tiredness, chest pain, and headache. Dermal, mucosal, or inhalation exposure can cause irritation.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to carbon black, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to carbon black at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• **Periodic medical screening and/or biologic monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to carbon black. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to carbon black may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to carbon black should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting carbon black particulate with tared 5 μm PVC membrane filters and analyzing by gravimetric methods. A detailed sampling and analytical method for carbon black may be found in the *NIOSH Manual of Analytical Methods* (method number 5000). Sam-

pling and analysis of PAH's present in the particulate or the filters may be performed by extracting with cyclohexane (aided by sonification), filtering through a fritted glass funnel, and weighing a dried aliquot of the extract. A detailed sampling and analytical method for cyclohexane-extractable PAH's may be found in *Criteria for a Recommended Standard. . . .Occupational Exposure to Carbon Black*.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with carbon black.

Workers should be provided with and required to use dust-proof safety goggles where carbon black may come in contact with the eyes.

SANITATION

Clothing which is contaminated with carbon black should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of carbon black from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of carbon black's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with carbon black should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle carbon black should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to carbon black may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for carbon black

Operations	Controls
During the manufacture of natural and synthetic rubber, dry cells, explosives, plastics, and paper	Local exhaust ventilation, personal protective equipment
During the manufacture and distribution of carbon black; during maintenance of equipment and storage containers	Local exhaust ventilation, personal protective equipment
During the manufacture and use of coatings and printing inks; during use as a coloring pigment and source of carbon	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to carbon black, an eye-wash fountain should be provided within the immediate work area for emergency use.

If carbon black gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to carbon black containing PAH's, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If carbon black gets on the skin, wash it immediately with soap and water. If carbon black penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If carbon black is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Carbon black dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods; it should then be placed in an appropriate container. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Tables 3 and 4).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respirator protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed in Table 3. All respirators that have higher protection factors may also be used. Table 4 lists respirators for protection against carcinogens, which includes only those respirators providing the highest protection factor available.

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Table 3.—Respiratory protection for carbon black

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 17.5 mg/m³	Any dust and mist respirator
Less than or equal to 35 mg/m³	Any dust and mist respirator except single-use and quarter-mask respirators
	Any supplied-air respirator
	Any air-purifying respirator with a high-efficiency particulate filter
	Any self-contained breathing apparatus
Less than or equal to 87.5 mg/m³	Any powered air-purifying respirator with a dust and mist filter
	Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 175 mg/m³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 3,500 mg/m³	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 3,500 mg/m³	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 3.5 mg/m³ (TWA).

Table 4.—Respiratory protection for carbon black containing greater than 0.1% PAH's

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for Carbon Dioxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CO_2
- Synonyms: Carbonic acid gas; "Dry Ice"; CO_2
- Appearance and odor: Primarily a colorless, odorless gas; however, it can be a liquid or a solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon dioxide is 5000 parts of carbon dioxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 9000 milligrams of carbon dioxide per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be changed to 10,000 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 30,000 ppm averaged over a 10-minute period. The NIOSH Criteria Document for Carbon Dioxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon dioxide can affect the body if it is inhaled. Solid carbon dioxide (dry ice) and compressed carbon dioxide gas from a cylinder can affect the body if it comes in contact with the eyes, skin, or mouth.

- **Effects of overexposure**

Inhaling carbon dioxide may cause rapid breathing, rapid beating of the heart, headache, sweating, shortness of breath, dizziness, mental depression, visual disturbances, shaking, unconsciousness, and death. Skin, eye, or mouth contact with solid carbon dioxide (dry ice) may cause frostbite. Similar effects may occur from carbon dioxide as it is being released from a cylinder.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon dioxide.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to carbon dioxide at potentially hazardous levels.

- **Summary of toxicology**

Carbon dioxide gas is an asphyxiant, a potent respiratory stimulant, and both a stimulant and depressant of the CNS. Respiratory volume is doubled at 4% CO_2 and redoubled at 5%. Increases in heart rate and blood pressure have been noted at 7.6% and dyspnea, headache, dizziness, and sweating occur if exposure at that level is prolonged. At 10% and above, prolonged exposure can result in unconsciousness. Above 11%, unconsciousness occurs in 1 minute or less. Numerous human fatalities have occurred after persons entered fermentation vats, wells, and silos where oxygen had been largely replaced by carbon dioxide. Exposure to very high concentrations, 25 to 30%, may cause convulsions. Carbon dioxide at room temperature will not injure the skin, but frostbite may result from contact with the solid or the liquid phases.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44
2. Boiling point (760 mm Hg): −78.5 C (−109 F) (sublimation point)
3. Specific gravity (water = 1): 1.02 (liquid)
4. Vapor density (air = 1 at boiling point of carbon dioxide): 1.52
5. Melting point: −78.5 C (-109 F) (sublimation point)
6. Vapor pressure at 20 C (68 F): Greater than 1

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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atmosphere

7. Solubility in water, g/100 g water at 20 C (68 F): 0.14

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None

2. Incompatibilities: Contact with chemically active metals such as sodium, potassium, or hot titanium may cause fire.

3. Hazardous decomposition products: None

4. Special precautions: Liquid or solid carbon dioxide will attack some forms of plastics, rubber, and coatings. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that carbon dioxide is an odorless gas.

2. Irritation Levels: Grant states that "carbon dioxide at high concentration in air causes a stinging sensation in the eyes, nose, and throat . . . ."

3. Evaluation of Warning Properties: Since carbon dioxide has no odor, and since no quantitative information is available relating its irritant effects of to air concentrations, this gas has been treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon dioxide. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of carbon dioxide in a gas sampling bag, followed by gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon dioxide may be used. An analytical method for carbon dioxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with solid carbon dioxide or from contact with vessels containing carbon dioxide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon dioxide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fermentation in manholes, mine floors, wells, shipwells, brewery vats, garbage dumps, and fruit storage facilities	General dilution ventilation; local exhaust ventilation; personal protective equipment

Operation	Controls
Use in cooling and refrigerating for storage, preparation and transfer of foods; use as an inert gas in fire extinguishers; for protection of flammable materials during manufacture; in shielded arc welding; and in canned food production	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an inert pressure medium for aerosol packaging; pressure spraying, spray painting, gas-operated firearms, purging tanks and pipelines, inflating liferafts, manufacture of plastic foam	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of carbonated beverages	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a neutralizing agent in textile processing and treatment of leather hides; use as shattering agent for coal mining; in fracturing and acidizing treatment of oil and gas wells	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use during water treatment for neutralizing alkaline waste waters; carbonating water to prevent scaling; use for chemical synthesis and pH control in manufacture of urea, asprin, carbonates and bicarbonates, beer, and sugar	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in miscellaneous operations for enrichment of greenhouse air, antiseptic, industrial solvent extraction, medical use, in foundries, cement curing, and in animal slaughter	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If solid carbon dioxide (dry ice) or carbon dioxide as it is being released from a cylinder gets into the eyes, get medical attention.

- **Skin or Mouth Exposure**

If solid carbon dioxide (dry ice) or carbon dioxide as it is being released from a cylinder comes in contact with the skin or mouth, stop the exposure immediately. If frostbite has occurred, get medical attention.

- **Breathing**

If a person breathes in large amounts of carbon dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If carbon dioxide is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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RESPIRATORY PROTECTION FOR CARBON DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 5000 ppm
Gas Concentration	
50,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 50,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Carbon Disulfide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CS_2
- Synonyms: Carbon bisulfide
- Appearance and odor: Colorless to faintly yellow liquid with a strong, disagreeable or sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon disulfide is 20 parts of carbon disulfide per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 30 ppm, and an acceptable peak of 100 ppm for 30 minutes in an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 1 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 10 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Carbon Disulfide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon disulfide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of carbon disulfide vapor may cause headache, nausea, drop in blood pressure, dizziness, unconsciousness, and death. Liquid carbon disulfide and high concentrations of the vapor may cause irritation of the skin, eyes, and nose. If the liquid is trapped under clothing, it may cause a burn. Swallowing carbon disulfide may cause loss of consciousness and convulsions. If small amounts are swallowed, vomiting, diarrhea, and headache may occur.

2. Long-term Exposure: Prolonged or repeated exposure to carbon disulfide may damage the nervous system and cause muscle weakness, numbness, feelings of pins and needles, unsteady walking, and difficulty in swallowing. Palsy, speech difficulty, and muscle spacticity may also occur. In addition, memory loss, headache, difficulty in sleeping, nervousness, fatigue, irritability, depression, suicidal tendencies, and psychosis may occur. Eye damage may occur with such symptoms as blind spots, narrowing of vision, and decreased ability to see in the dark. Increased arteriosclerosis may occur which may cause or increase damage to the heart and other organs. High blood pressure, kidney damage, liver damage, and stomach problems may occur. Repeated or prolonged exposure of the skin to carbon disulfide may cause a skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon disulfide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to carbon disulfide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems, eyes, cardiovascular system, kidneys, and liver should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to carbon disulfide, a urinalysis

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Since liver damage has been observed in humans exposed to carbon disulfide, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—An electrocardiogram: Carbon disulfide has caused arrhythmias and electrocardiographic changes in humans. Periodic surveillance is indicated.

—Ophthalmic examination: Carbon disulfide has caused ocular changes in humans. An ophthalmic examination should be performed, including visual acuity.

—Medical warning: Workers should be informed of potential undesirable effects of exposure to carbon disulfide on reproduction (such as spermatic deficiences, menstrual disorders, and spontaneous abortions).

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Carbon disulfide vapor causes narcosis at high concentrations; repeated exposure to low concentrations causes damage to the central and peripheral nervous systems and may accelerate the development of or worsen coronary heart disease. Exposure of humans to 1150 ppm causes serious symptoms, and 4800 ppm for 30 minutes may be fatal. Carbon disulfide intoxication can involve all parts of the central and peripheral nervous systems, including damage to the cranial nerves and development of polyneuritis with paresthesias and muscle weakness in the extremities, unsteady gait, and dysphagia. In extreme cases of intoxication, a Parkinson-like syndrome may result, characterized by speech disturbances, muscle spasticity, tremor, memory loss, mental depression, and marked psychic symptoms; permanent disability is likely. Reproductive disorders occur, such as aspermia, menstrual irregularities, and spontaneous abortion. Psychosis and suicide are established risks of overexposure to carbon disulfide. Other reported effects of exposure to carbon disulfide are ocular changes (retinal degeneration, corneal opacities, disturbances of color vision, corneal anesthesia, diminished pupillary reflexes, microscopic aneurysms in the retina), gastrointestinal disturbances (chronic gastritis and achlorhydria), renal impairment (albuminuria, microhematuria, elevated blood urea nitrogen, diastolic hypertension), and liver damage. Effects commonly caused by repeated exposure to carbon disulfide vapor are exemplified by a group of workers with a time-weighted average (TWA) exposure of 11.2 ppm (range 0.9 to 127 ppm) who complained of headaches and dizziness; in other workers with a TWA of 186 ppm (range 23 to 378 ppm) complaints also included sleep disturbances, fatigue, nervousness, anorexia, and weight loss; the end-of-day exposure coefficient of the iodine azide test on urine was a good indicator of workers who were or had been symptomatic. Overexposure to carbon disulfide has long been regarded as potentially atherogenic for cerebral, renal, and coronary arteries; recent epidemiologic studies of viscose rayon workers have confirmed a 2.5- to 5-fold increase in risk of death from coronary heart disease as compared with the experience of unexposed workers. Other cardiovascular effects observed in workers repeatedly exposed to carbon disulfide are bradycardia, tachycardia, arrhythmias, and electrocardiographic changes consistent with both nonspecific and ischemic wave changes. Splashes of the liquid in the eyes cause immediate and severe irritation; dermatitis and vesiculation may result from skin contact with the vapor or the liquid. Although ingestion is unlikely to occur, it may cause coma and convulsions.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76.1
2. Boiling point (760 mm Hg): 46.3 C (115 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of carbon disulfide): 2.6
5. Melting point: −111.5 C (-169 F)
6. Vapor pressure at 20 C (68 F): 300 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): 22.6

- **Reactivity**

1. Conditions contributing to instability: Containers may burst when heated.
2. Incompatibilities: Contact with strong oxidizers, and chemically active metals (such as sodium, potassium, and zinc), azides, and organic amines may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide and carbon monoxide) may be released in a fire involving carbon disulfide.
4. Special precautions: Liquid carbon disulfide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −30 C (-22 F) (closed cup)
2. Autoignition temperature: 90 C (194 F)
3. Flammable limits in air, % by volume: Lower: 1.3; Upper: 50
4. Extinguishant: Dry chemical, carbon dioxide for small fires

- **Warning properties**

1. Odor Threshold: The *Handbook of Organic Industrial Solvents* states that at less than 1 ppm, carbon disulfide has a disagreeable odor. Summer gives an odor threshold of 7.7 ppm , and May gives 0.0011 ppm and 0.0081 ppm. The AIHA *Hygienic Guide* gives an odor threshold of 1.2 ppm.
2. Eye Irritation Level: Carbon disulfide is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of carbon disulfide is below the permissible

exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon disulfide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of carbon disulfide. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of carbon disulfide vapors using an adsorption tube with subsequent desorption with benzene and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon disulfide may be used. An analytical method for carbon disulfide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid carbon disulfide, where skin contact may occur.

• Non-impervious clothing which becomes contaminated with carbon disulfide should be removed promptly and not reworn until the carbon disulfide is removed from the clothing.

• Any clothing which becomes wet with liquid carbon disulfide should be removed immediately and not reworn until the carbon disulfide is removed from the clothing.

• Clothing wet with liquid carbon disulfide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of carbon disulfide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the carbon disulfide, the person performing the operation should be informed of carbon disulfide's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where liquid carbon disulfide may contact the eyes.

SANITATION

• Skin that becomes contaminated with carbon disulfide should be promptly washed or showered with soap or mild detergent and water to remove any carbon disulfide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon disulfide may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of viscose rayon during xanthation of cellulose and spinning and cutting operations; use as a xanthating agent in manufacture of cellophane; use during manufacture of pesticides	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use as a fumigant and spray application on grains, and space fumigation of agricultural premises	General dilution ventilation; temperature control; personal protective equipment
Use in synthesis of carbon tetrachloride	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use in synthesis of intermediates and manufacture of dyes, pharmaceuticals, rubber chemicals, pesticides, and flotation agents	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Liberation during destructive distillation of coal in manufacture of coal gas and coal tar	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use as a solvent in dry spinning of polyvinyl chloride; as a solvent in oil wells; use in manufacture of optical glass	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use during rubber manufacture in cold curing operations; during extraction processing of oils, fats, resins, and waxes; use in manufacture of matches	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid carbon disulfide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid carbon disulfide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid carbon disulfide soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention promptly.

• **Breathing**

If a person breathes in large amounts of carbon disulfide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When liquid carbon disulfide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If carbon disulfide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Carbon disulfide should not be allowed to enter a confined space, such as

a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of carbon disulfide vapors are permitted.

• Waste disposal method:

Carbon disulfide may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR CARBON DISULFIDE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Vapor Concentration	
200 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
500 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Carbon Monoxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CO
- Synonyms: Monoxide
- Appearance and odor: Colorless, odorless gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon monoxide is 50 parts of carbon monoxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 55 milligrams of carbon monoxide per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 35 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 200 ppm. The NIOSH Criteria Document for Carbon Monoxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon monoxide can affect the body if it is inhaled or if liquid carbon monoxide comes in contact with the eyes or skin.

- **Effects of overexposure**

Exposure to carbon monoxide decreases the ability of the blood to carry oxygen to the tissues. Inhalation of carbon monoxide may cause headache, nausea, dizziness, weakness, rapid breathing, unconsciousness, and death. High concentrations may be rapidly fatal without producing significant warning symptoms. Exposure to this gas may aggravate heart disease and artery disease and may cause chest pain in those with pre-existing heart disease. Pregnant women are more susceptible to the effects of carbon monoxide exposure. The effects are also more severe in people who are working hard and in people who are working in places where the temperature is high or at altitudes above 2,000 feet. Skin exposure to liquid carbon monoxide may cause frostbite-type burns.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon monoxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to carbon monoxide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of coronary heart disease, anemia, pulmonary heart disease, cerebrovascular disease, thyrotoxicosis, and smokers would be expected to be at increased risk from exposure. Pregnant women have an increased sensitivity to the effects of carbon monoxide. Examination of the cardiovascular system, the pulmonary system, the blood, and the central nervous system should be stressed.

—A complete blood count: Carbon monoxide affects the ability of the blood to carry oxygen. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception that a carboxyhemoglobin determination should be performed at any time overexposure is suspected or signs or symptoms of toxicity occur.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

• **Summary of toxicology**

Carbon monoxide (CO) gas causes tissue hypoxia by preventing the blood from carrying sufficient oxygen. CO combines reversibly with the oxygen-carrying sites on the hemoglobin molecule with an affinity ranging from 210 to 240 times greater than that of oxygen; the carboxyhemoglobin thus formed is unavailable to carry oxygen. In addition, carboxyhemoglobin interferes with the release of oxygen carried by unaltered hemoglobin. With exposure to high concentrations such as 4000 ppm and above, transient weakness and dizziness may be the only premonitory warnings before coma supervenes; the most common early aftermath of severe intoxication is cerebral edema. Exposure to concentrations of 500 to 1000 ppm causes the development of headache, tachypnea (rapid breathing), nausea, weakness, dizziness, mental confusion, and in some instances, hallucinations, and may result in brain damage. The affected person is commonly cyanotic. Concentrations as low as 50 ppm result in blood COHb levels up to 10% in an 8-hour day. This greatly increases the risk of angina pectoris and coronary infarctions by decreasing the oxygen supply in the blood and also in the myoglobin of the heart muscle. These effects are aggravated by heavy work, high ambient temperatures, and high altitudes. Pregnant women are especially susceptible to the effects of increased CO levels. Smoking also increases the risk: cigarette smoke contains 4% CO, which results in 5.9% COHb if a pack a day is smoked. The blood of persons not exposed to CO contains about 1% CO, probably as a result of normal heme metabolism. The diagnosis of CO intoxication depends primarily on the demonstration of significantly increased carboxyhemoglobin in the blood. Levels over 60% are usually fatal; 40% is associated with collapse and syncope; above 25% there may be electrocardiographic evidence of a depression of the S-T segment; between 15% and 25% there may be headache and nausea. The reaction to a given blood level of carboxyhemoglobin is extremely variable: some persons may be in coma with a carboxyhemoglobin level of 38% while others may maintain an apparently clear sensorium with levels as high as 55%. The blood of cigarette smokers contains 3 to 10% carboxyhemoglobin, and nonexposed persons have an average level of 1%, probably as a result of normal heme metabolism. Several investigators have suggested that the results of behavioral tests such as time discrimination, visual vigilance, choice response tests, visual evoked responses, and visual discrimination thresholds may be altered at levels of carboxyhemoglobin below 5%.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 28
2. Boiling point (760 mm Hg): −191.5 C (-313 F)
3. Specific gravity (water = 1): 0.79 (liquid at boiling point)
4. Vapor density (air = 1 at boiling point of carbon monoxide): 0.97
5. Melting point: −199 C (-326 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.004
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to explode.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: 609 C (1128 F)
3. Flammable limits in air, % by volume: Lower: 12.5; Upper: 74
4. Extinguishant: Dry chemical. If flow of gas cannot be stopped, let fire burn.

• **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* points out that carbon monoxide is odorless.
2. Eye Irritation Level: Grant states that carbon monoxide is a non-irritating gas.
3. Evaluation of Warning Properties: Carbon monoxide is an odorless, non-irritating gas. It has no warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon monoxide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of carbon monoxide vapors using an adsorption tube with a subsequent chemical analysis of the adsorption

tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon monoxide may be used. An analytical method for carbon monoxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid carbon monoxide or from contact with vessels containing liquid carbon monoxide.

• Any clothing which becomes wet with liquid carbon monoxide should be removed immediately and not reworn until the carbon monoxide has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid carbon monoxide may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon monoxide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from emissions in enclosed places from exhaust fumes of internal combustion engines; from metallurgic industry and foundries; from chemical industry for synthesis and emission as result of incomplete combustion	Local exhaust ventilation; respiratory protective device
Liberation during acetylene welding; from enclosed areas as mines or tunnels; from fire-damp explosions	Local exhaust ventilation; respiratory protective device
Liberation from industrial heating	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Breathing**

If a person breathes in large amounts of carbon monoxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks or releases until cleanup has been completed.

• If carbon monoxide is leaked or released in hazardous concentrations, the following steps should be taken:
1. Ventilate area of leak or release to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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- Zenz, C.: *Occupational Medicine – Principles and Practical Applications*, Year Book Medical, Inc., Chicago, 1975.

RESPIRATORY PROTECTION FOR CARBON MONOXIDE

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Gas Concentration	
500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 1500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against carbon monoxide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBON TETRABROMIDE

INTRODUCTION

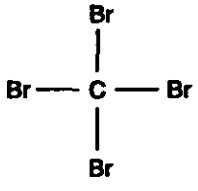
This guideline summarizes pertinent information about carbon tetrabromide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CBr_4

- **Structure**



- **Synonyms**

  Carbon bromide, tetrabromomethane, methane tetrabromide

- **Identifiers**

  1. CAS No.: 558-13-4
  2. RTECS No.: FG4725000
  3. DOT UN: 2516 53
  4. DOT label: St. Andrew's Cross

- **Appearance and odor**

  Carbon tetrabromide is a nonflammable, colorless to yellow-brown, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 331.65
  2. Boiling point (760 mm Hg): 189.5°C (373.1°F)
  3. Specific gravity (water = 1): 3.42
  4. Vapor density (air = 1 at boiling point of carbon tetrabromide): 11.4
  5. Melting point: 90.1°C (194.2°F)
  6. Vapor pressure at 96.3°C (205°F): 40 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol, ether, chloroform, and other organic solvents
  8. Evaporation rate: Data not available

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National Institute for Occupational Safety and Health
Education and Information Division

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Occupational Safety and Health Administration

Reactivity

1. Conditions contributing to instability: None reported

2. Incompatibilities: Contact of carbon tetrabromide with lithium or hexylcyclohexyldilead may cause an explosion.

3. Hazardous decomposition products: Toxic gases (such as bromine) may be released in a fire involving carbon tetrabromide.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to carbon tetrabromide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or regular foam.

Fires involving carbon tetrabromide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbon tetrabromide. Structural firefighters' protective clothing may provide limited protection against fires involving carbon tetrabromide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for carbon tetrabromide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (1.4 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.3 ppm (4 mg/m^3) as a STEL. A STEL is a 15-min TWA exposure that should not be exceeded at any time during the workday [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbon tetrabromide a threshold limit value (TLV) of 0.1 ppm (1.4 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (4.1 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The NIOSH limits are based on the risk of eye, skin, lung, and liver irritation, and hepatotoxic effects associated with exposure to carbon tetrabromide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbon tetrabromide can occur through inhalation, eye or skin contact, and ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbon tetrabromide is a severe irritant of the eyes and respiratory tract as well as a liver and kidney toxicant. Undiluted carbon tetrabromide applied to the eyes of rabbits caused severe irritation and permanent corneal damage. However, when the material was promptly washed from the eyes, pain and irritation were noted but the corneal damage was reversible. Exposure of rats to carbon tetrabromide fume at 10 mg/m^3 for 4 hr daily caused irritation of the eyes and respiratory tract [Clayton and Clayton 1981]. Contact with the skin of rabbits caused relatively slight irritation, but when the material was confined tightly to the skin, it caused hyperemia and a moderate degree of swelling [Clayton and Clayton 1981]. The subcutaneous LD_{50} in mice is 298 mg/kg [NIOSH 1992b] and the rat oral

LD_{50} is 1,800 mg/kg [Clayton and Clayton 1981]. Rats exposed to 10 to 1,000 mg/m^3 (0.07 to 74 ppm) for 4 hr/day during a 4-month period exhibited metabolic changes in the liver [Clayton and Clayton 1981]. Rats repeatedly exposed to 100 mg/m^3 or to 300 to 500 mg/m^3 (depending on the analytical method) for 7 hr/day, 5 days/week during a 6-month period showed no effects, but exposure to higher (not further specified) concentrations caused poor growth; fatty and degenerative changes of the liver appeared at autopsy [Clayton and Clayton 1981].

2. *Effects on Humans:* Carbon tetrabromide is a severe irritant of the eyes, nose, throat, and lungs; it is also a liver toxicant. The vapor of carbon tetrabromide causes pronounced eye irritation and lacrimation even at low concentrations [Clayton and Clayton 1981]. Exposure to high concentrations (not further specified) of carbon tetrabromide vapors can irritate the upper respiratory tract, cause CNS depression, and injure the lungs, liver, and kidneys [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to carbon tetrabromide can induce corneal damage, profuse tearing and burning of the eyes; ocular, skin, and upper respiratory tract irritation; and CNS depression.

2. *Chronic exposure:* Liver damage is the primary response to chronic exposure to carbon tetrabromide at very low concentrations [Clayton and Clayton 1981]. Chronic exposure to low concentrations of carbon tetrabromide can also induce contact irritation.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritaiton!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of carbon tetrabromide. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbon tetrabromide or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

Workers may be exposed to carbon tetrabromide during its use as an intermediate in the manufacture of other chemicals.

The following methods are effective in controlling worker exposures to carbon tetrabromide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to carbon tetrabromide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and liver.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbon tetrabromide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or liver.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbon tetrabromide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbon tetrabromide on the eyes, skin, and liver. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for carbon tetrabromide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's

health status should be compared with those expected for a suitable reference population. Because occupational exposure to carbon tetrabromide may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbon tetrabromide is determined by using an XAD-4 tube (80/40-mg sections, 15/50 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 10 liters (TWA) or 3 liters (STEL) is collected. The sample is then treated with toluene to extract the carbon tetrabromide. Analysis is conducted by gas chromatography using an electron capture detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If carbon tetrabromide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with carbon tetrabromide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of carbon tetrabromide, particularly its potential to cause burns of the eyes and skin.

A worker who handles carbon tetrabromide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbon tetrabromide or a solution containing carbon tetrabromide is handled, processed, or stored.

STORAGE

Carbon tetrabromide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbon tetrabromide should be protected from physical damage and should be stored separately from strong oxidizers, lithium, hexylcyclohexyldilead, heat, sparks, and open flame. Because containers that formerly contained carbon tetrabromide may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving carbon tetrabromide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Use a clean shovel and gently place the spilled material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbon tetrabromide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 CFR 355.40] to notify the National Response Center of an accidental release of carbon tetrabromide; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbon tetrabromide emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although carbon tetrabromide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbon tetrabromide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, gauntlets, aprons, coveralls, and other clothing, as appropriate) should be worn to prevent any skin contact with carbon tetrabromide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. A Viton/neoprene laminate has been tested against carbon tetrabromide and has demonstrated good resistance. A laminate of butyl rubber and neoprene has demonstrated poor resistance to permeation by carbon tetrabromide.

If carbon tetrabromide is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbon tetrabromide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbon tetrabromide. Contact lenses should not be worn if the potential exists for carbon tetrabromide exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBON TETRACHLORIDE

INTRODUCTION

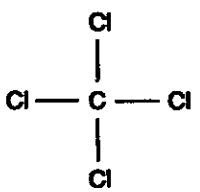
This guideline summarizes pertinent information about carbon tetrachloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

CCl_4

- **Structure**



- **Synonyms**

Tetrachloromethane; perchloromethane; methane tetrachloride; Nectorina; benzinoform; carbon chloride; Carbona; carbon tet

- **Identifiers**

1. CAS No.: 56-23-5
2. RTECS No.: FG4900000
3. DOT UN: 1846 55
4. DOT label: Poison

- **Appearance and odor**

Carbon tetrachloride is a noncombustible, colorless liquid with a sweet, aromatic, etherlike odor. The best estimate of the odor threshold for carbon tetrachloride is 250 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 153.84
2. Boiling point (760 mm Hg): 76.7°C (170°F)
3. Specific gravity (water = 1): 1.59 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of carbon tetrachloride): 5.3
5. Melting point: –23°C (–9.4°F)
6. Vapor pressure at 20°C (68°F): 91.3 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; miscible with alcohol, benzene, chloroform, ether, carbon disulfide, petroleum ether, and oils

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: None reported

2. Incompatibilities: Contact of carbon tetrachloride with fluorine gas, alkali metals, or aluminum may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as phosgene and hydrogen chloride) may be released in a fire involving carbon tetrachloride. When used to put out electrical fires, carbon tetrachloride may evolve phosgene gas.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to carbon tetrachloride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is appropriate for the materials involved in the surrounding fire.

Fires involving carbon tetrachloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbon tetrachloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Fire fighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbon tetrachloride. Chemical protective clothing that is specifically recommended for carbon tetrachloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural Fire fighters' protective clothing is not effective against fires involving carbon tetrachloride.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for carbon tetrachloride is 10 ppm as an 8-hr time-weighted average (TWA) concentration with a ceiling concentration of 25 ppm that may not be exceeded during an 8-hr workday except for a 5-min period every 4 hours; the acceptable maximum peak during this 5-min period is 200 ppm [29 CFR 1910.1000, Table Z-2].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) designates carbon tetrachloride a potential occupational carcinogen and has established a recommended exposure limit (REL) for this substance of 2 ppm (12.6 mg/m^3) as a 60-min short-term exposure limit (STEL) [NIOSH 1992a]. The STEL is a 60-min TWA exposure that shall not be exceeded at any time during a workday.

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has designated carbon tetrachloride an A2 substance (suspected human carcinogen) and has assigned carbon tetrachloride a threshold limit value (TLV) of 5 ppm (31 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned carbon tetrachloride a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cancer associated with exposure to carbon tetrachloride [ACGIH 1993; NIOSH 1992a].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbon tetrachloride can occur through inhalation of the vapor, eye or skin contact, absorption through the skin of the liquid, or ingestion.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, carbon tetrachloride is an eye and skin irritant, a liver and kidney toxin, and a carcinogen. This chemical is a mild eye and skin irritant in rabbits [NIOSH 1992b]. Monkeys demonstrated little dermal absorption from ambient exposures. Likewise, rats dermally exposed to the liquid required large doses to induce lethality [Clayton and Clayton 1981]. The dermal LD_{50} in rats is 5,070 mg/kg [NIOSH 1992b]. The maximum exposures that caused no effects in male rats were: 3,000 ppm for 6 min, 800 ppm for 30 min, and 50 ppm for 7 hr [Clayton and Clayton 1981]. The highest airborne concentrations in which rats survived were 12,000 ppm for 15 min and 3,000 ppm for 8 hr [Clayton and Clayton 1981]. The LC_{50} in rats and mice are 8,000 ppm for 4 hr and 9,526 ppm for 8 hr, respectively [NIOSH 1992b]. The oral LD_{50} in rats is 2,350 mg/kg [NIOSH 1992b]. Rats, guinea pigs, rabbits, and monkeys were exposed to carbon tetrachloride vapors for 7 hr/day, 5 days/week for up to 4 months. Rats, guinea pigs, and rabbits all showed histologic damage to the liver after exposures of 10 ppm or higher but not after exposure to 5 ppm; monkeys exhibited histologic damage to the liver at concentrations of 100 ppm or above but not at lower levels [Clayton and Clayton 1981]. Carbon tetrachloride was embryotoxic and fetotoxic but not teratogenic in rats exposed to 300 to 1,000 ppm for 7 hr/day on days 6 to 15 of gestation [IARC 1979; NIOSH 1992b]. This chemical also increased fetal mortality when pregnant mice were given a single 150 mg dose [IARC 1979]. Carbon tetrachloride is weakly mutagenic in a wide variety of test systems [NIOSH 1992b]. This chemical produced liver tumors as well as cancers in mice, rats, and hamsters following administration by several routes, including inhalation and ingestion [ACGIH 1991; IARC 1979]. The International Agency for Research on Cancer (IARC) has determined that there is sufficient evidence of carbon tetrachloride's carcinogenicity in animals and that it is a Group 2B carcinogen (possibly carcinogenic in humans) [IARC 1987].

2. *Effects on Humans:* In humans, carbon tetrachloride is a mild eye and skin irritant, a central nervous system depressant, and a liver and kidney toxin. NIOSH, ACGIH, and other organizations classify carbon tetrachloride as a potential human carcinogen. The vapor of carbon tetrachloride is mildly irritating to the eyes [Grant 1986]; and has also caused visual disturbances (concentric restriction of color fields) [NLM 1991]. Prolonged or repeated contact of the liquid with the skin can cause pain, erythema, hyperemia, weal formation, tissue defatting and blistering [Grant 1986; Hathaway et al. 1991; NLM 1991]. The estimated no-observed-effect level for acute human exposure is 10 ppm for 3 hr [Hathaway et al. 1991]. A TC_{Lo} (lowest concentration causing an effect) exposure of 20 ppm (duration undefined) or 317 ppm for 30 min has produced nausea and vomiting [NIOSH 1992b]. Acute symptoms can include abdominal cramps, nervousness, dyspnea, cyanosis, oliguria, proteinuria, hepatomegaly, and optic neuritis [NIOSH 1992b]. Polycythemia, anemia, and hemodilution also may follow acute exposure [Hathaway et al. 1991]. Mild acute poisoning can result in renal injury, and decreased renal blood flow and filtration, which may require up to 200 days for complete recovery. In severe acute poisoning, anuria and terminal uremia require active restoration of renal function, or death occurs [NLM 1991]. In humans, the majority of fatalities caused by inhalation of carbon tetrachloride have been the result of renal injury with secondary cardiac failure. Liver damage occurs more often from ingestion of the liquid than from inhalation of the vapor [Hathaway et al. 1991]. Persons consuming alcohol, those with poor nutritional status, and persons with pre-existing liver or kidney disease are more susceptible to poisoning by carbon tetrachloride [Gosselin et al. 1984]. Human fatalities caused by acute renal failure have resulted from exposure to carbon tetrachloride concentrations of 50,000 ppm for 5 min [NLM 1991], 1,000 to 2,000 ppm for 30 min to 1 hr [Hathaway et al. 1991], or oral doses that exceed 1,500 mg/kg [NIOSH 1992b]. Although repeated exposure of workers to 10 ppm did not induce signs or symptoms of toxicity, 25 to 30 ppm caused nausea, vomiting, dizziness, drowsiness, and headache [NLM 1991]. Ten out of 17 workers exposed for an unspecified period to a 45- to 97-ppm concentration of carbon tetrachloride reported experiencing headache and giddiness, and several of these workers also had symptoms of liver dysfunction [ACGIH 1991]. Workers exposed to carbon tetrachloride at unspeci-

fied levels have experienced dizziness, vertigo, mental confusion, and incoordination, all signs and symptoms of central nervous system depression, and some have developed loss of visual acuity, convulsions, and cardiac arrhythmias [Hathaway et al. 1991]. Carbon tetrachloride has been confirmed as a weak mutagen in a variety of assays [NIOSH 1992b]. In the preamble of the 1989 *Air Contaminants; Final Rule,* OSHA concluded that an "occupational exposure to carbon tetrachloride at the 10-ppm PEL presents a significant risk of cancer to workers" [54 Fed. Reg. 2681 (1989)]. IARC has concluded that there is insufficient human data to directly classify carbon tetrachloride's carcinogenic risk to humans [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbon tetrachloride can induce mild irritation of the eyes and skin, with redness and inflammation, and central nervous system depression, with symptoms of malaise, headache, dizziness, incoordination, confusion, stupor, coma, and convulsions; nausea, vomiting, abdominal pain, and diarrhea are also frequent. Acute exposures can lead to ventricular fibrillation (rapid, irregular heartbeat) and death from cardiac failure. Acute oral exposures have primarily caused liver damage, as evidenced by an ehlarged and tender liver and jaundice, as well as acute nephritis, with a decrease in the volume of urinary output and the presence of blood, pus, or protein in the urine. Acute renal failure can result in coma and death.

2. *Chronic exposure:* Repeated contact of the skin with carbon tetrachloride may cause defatting of the skin and dermatitis, with redness and blister formation. Chronic exposure has also been associated with nausea, vomiting, dizziness, drowsiness, headache, visual disturbances, and loss of visual acuity. The IARC classifies carbon tetrachloride as possibly carcinogenic to humans based on sufficient animal data.

- **Emergency procedures**

> WARNING!
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of carbon tetrachloride. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if carbon tetrachloride or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by touching the back of the throat with a finger until productive vomiting ceases. Do ***not*** give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbon tetrachloride and result in worker exposures to this substance:

—Manufacture of fluorocarbons for aerosols, refrigerants, and fire extinguishants (these uses of fluorocarbons have been largely phased out or banned)

—Use as a solvent in dry cleaning and in industry to dissolve resins, oils, fats, varnishes, and rubber waxes

—Use as an agricultural grain fumigant, pesticide, and anthelmintic and as an agent to extract oil from flowers and seeds

—Use in polymer technology as a reaction medium, catalyst, and chain transfer agent

—Use in organic synthesis for the chlorination of organic compounds and in the soap and perfume industries

—Use as a laboratory solvent

—Use in tin recovery and catalyst regeneration and as a cleaning agent for machinery and electrical equipment

The following methods are effective in controlling worker exposures to carbon tetrachloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to carbon tetrachloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and nervous system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbon tetrachloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of excessive alcohol intake and other findings consistent with diseases of the liver, kidney, or nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the

employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbon tetrachloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbon tetrachloride on the liver, kidneys, or nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although carbon tetrachloride can be detected in the breath of exposed workers, data on the correlation between breath concentrations and airborne concentrations of carbon tetrachloride are not available. Therefore, no biological monitoring test acceptable for routine use has yet been developed for carbon tetrachloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to carbon tetrachloride may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbon tetrachloride is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a maximum air volume of 15 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg, and the method is described in NIOSH Method No. 1003 [NIOSH 1984].

PERSONAL HYGIENE

This substance can be absorbed through the skin in toxic amounts. Therefore, if carbon tetrachloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with carbon tetrachloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of carbon tetrachloride, particularly its potential to cause severe central nervous system effects on acute exposure.

A worker who handles carbon tetrachloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbon tetrachloride is handled, processed, or stored.

STORAGE

Carbon tetrachloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of carbon tetrachloride should be protected from physical damage and direct sunlight and should be stored separately from aluminum, barium, dimethyl formamide, magnesium, potassium, sodium, triethylaluminum, calcium disilicide decaborane, ethylene, heat, sparks, and open flame. Because containers that formerly contained carbon tetrachloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving carbon tetrachloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Ventilate the area of the spill or leak.

4. Use water spray to reduce vapors.

5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the carbon tetrachloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbon tetrachloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbon tetrachloride is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of carbon tetrachloride per calendar year are required by EPA [49 CFR Part 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbon tetrachloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Carbon tetrachloride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 CFR 355.40], and has been assigned EPA Hazardous Waste No. U211. This chemical is approved for land disposal as long as the concentration of carbon tetrachloride in the waste or treatment residual does not exceed 5.6 mg/kg. Carbon tetrachloride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbon tetrachloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with carbon tetrachloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been recommended for use against permeation by carbon tetrachloride and may provide protection for periods greater than 8 hr: polyvinyl alcohol, Viton, Barricade®, and Responder®. Materials that may withstand permeation for more than 4 but fewer than 8 hr are Teflon and a polyethylene/ethylene vinyl laminate. Protective clothing made of butyl rubber, natural rubber, neoprene, nitrile rubber, polyethylene, or polyvinyl chloride are not recommended for protection against permeation by carbon tetrachloride.

If carbon tetrachloride is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which carbon tetrachloride might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbon tetrachloride. Contact lenses should not be worn if the potential exists for carbon tetrachloride exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CARBONYL FLUORIDE

INTRODUCTION

This guideline summarizes pertinent information about carbonyl fluoride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CF_2O

- **Synonyms**

  Carbon difluoride oxide, carbon fluoride oxide, carbon oxyfluoride, carbonyl difluoride, difluoroformaldehyde, fluoroformyl fluoride, fluorophosgene, carbonic difluoride

- **Identifiers**

  1. CAS No.: 353-50-4
  2. RTECS No.: FG6125000
  3. DOT UN: 2417 15
  4. DOT label: Poison Gas

- **Appearance and odor**

  Carbonyl fluoride is a noncombustible, colorless, hygroscopic gas with a pungent and very irritating odor. It is shipped as a liquefied gas under its own vapor pressure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 66.01
  2. Boiling point (760 mm Hg): -83°C (-117.6°F)
  3. Specific gravity (water = 1): 1.14 at -114°C (-173°F)
  4. Vapor density: Data not available
  5. Melting point: -114°C (-173°F)
  6. Vapor pressure at 21.1°C (70°F): 42,104 mm Hg
  7. Solubility: Instantly hydrolyzed by water; decomposes in alcohol
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Heat and moisture
  2. Incompatibilities: Contact with moisture causes the instantaneous hydrolysis of carbonyl fluoride to very corrosive and toxic hydrogen fluoride gas and carbon dioxide.

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National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases (such as oxides of fluorine and carbon) may be released in a fire involving carbonyl fluoride.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating to carbonyl fluoride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical or carbon dioxide for small fires; water spray, fog, or regular foam for large fires.

Fires involving carbonyl fluoride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of carbonyl fluoride may explode in the heat of the fire and should be removed if it is possible to do safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Do not get water inside the containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving carbonyl fluoride. Structural firefighters' protective clothing is not effective against fires involving carbonyl fluoride.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) had not promulgated a permissible exposure limit (PEL) for carbonyl fluoride [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (5 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 5 ppm (15 mg/m^3) as a STEL. A STEL is a 15 min exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned carbonyl fluoride a threshold limit value (TLV) of 2 ppm (5.4 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 5 ppm (13 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of irritation associated with exposure to carbonyl fluoride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to carbonyl fluoride can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Carbonyl fluoride gas causes severe contact irritation or corrosion of tissues following acute exposure. In the presence of humidity or tissue fluids, it is rapidly hydrolyzed to two moles of hydrofluoric acid which is primarily responsible for the toxic effects elicited in exposed subjects. A near-lethal acute exposure, 310 ppm for 1 hr, of sacrificed mice, rats, guinea pigs, rabbits, and dogs resulted in the following histological lung changes: focal hemorrhage and edema at 24 hr; cellular repair with decreased edema at 48 hr; repair of damaged alveolar capillaries before 7 days; and a small amount of irreversible focal emphysema and mild interstitial fibrosis at the terminal 3-week sacrifice. The LC_{50}s in rats are 360 ppm for 1 hr and 90 ppm for 4 hr [NIOSH 1991]. Death resulted from respiratory or cardiac failure [NIOSH 1991; Scheel et al. 1968a]. Rats were exposed to polytetrafluoroethylene (PTFE) pyrolysis products containing hydrolyzable fluoride equal to a 50-ppm concentration of carbonyl fluoride for 1 hr/day for 5 days. Daily urinary fluoride levels reached 14 times normal on the first exposure day and continued to be markedly elevated 18 days after exposure. The animals' body weights declined by 30%, urinary glucose, protein, and ketones became

abnormal, and succinic-dehydrogenase activity declined sharply in the kidney and rose sharply in the lung. Mortality among the rats exposed repeatedly to carbonyl fluoride was high (9 of 40), indicating that fluoride continued to be liberated by hydrolysis once in the body [Scheel et al. 1968b].

2. *Effects on Humans:* Carbonyl fluoride is a severe irritant of the eyes, skin, mucous membranes, and respiratory tract in humans. Its respiratory toxicity is believed to be equivalent to that of hydrogen fluoride [ACGIH 1993]. On repeated exposure, carbonyl fluoride inhibits succinic dehydrogenase activity, indicating that sublethal exposures are cumulative and that fluoride continues to be liberated after absorption into the body [Sittig 1985].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Carbonyl fluoride can cause pain, redness, and tearing of the eyes, eye or skin burns (corrosion), runny nose, coughing, pulmonary edema, and difficult breathing.

2. *Chronic exposure:* Carbonyl fluoride toxicity is similar to that caused in fluoride poisoning: respiratory distress, neurological abnormalities, gastrointestinal pain, muscular fibrillation, and skeletal fluorosis (excessive calcification of bone).

- **Emergency procedures**

> **WARNING!**
>
> **Exposed victims may die!**
> **Transport immediately to emergency medical facility**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* Severe burns and skin corrosion may result! If tissue is frozen, seek medical attention ***immediately***; do ***not*** rub the affected areas or flush them with water. If tissue is not frozen, ***immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve carbonyl fluoride and may result in worker exposures to this substance:

—Use in organic synthesis

—Thermal decomposition of polytetrafluoroethylene (Teflon, Fluon, etc.)

—Proposed use as a military poison gas

The following methods are effective in controlling worker exposures to carbonyl fluoride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to carbonyl fluoride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, respiratory system, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to carbonyl fluoride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to carbonyl fluoride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of carbonyl fluoride on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Urinary fluoride concentration is a useful index of fluoride intake in workers; at an airborne concentration of 2.5 g/m^3 inorganic fluoride, average end-of-shift (8 hr) urinary concentrations are 4 mg fluoride per liter of urine. Some sources recommend an end-of-shift biological exposure index (BEI) of 10 mg fluoride per gram creatinine and a preshift BEI of 3 mg fluoride per gram creatinine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected phys-

iologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne carbonyl fluoride is determined by using a midget fritted-glass bubbler containing 10 ml 0.1N sodium hydroxide. Samples are collected at a recommended flow rate of 2.0 liter/min until a recommended air volume of 480 liters is collected. Analysis is conducted using an ion specific electrode. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If carbonyl fluoride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with carbonyl fluoride should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles carbonyl fluoride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where carbonyl fluoride is handled, processed, or stored.

STORAGE

Carbonyl fluoride should be stored in a cool, dry, well-ventilated area in tightly sealed, pressurized containers or holding tanks that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. All piping systems in storage areas should be equipped with leak detection equipment to provide warning of leaks. Containers of carbonyl fluoride should be protected from physical damage and should be stored separately from moisture and heat.

LEAKS

In the event of a leak involving carbonyl fluoride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the leak.
5. For small spills, flush area with flooding amounts of water.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Carbonyl fluoride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for carbonyl fluoride is 1,000 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will

expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

Community right-to-know requirements

Employers are not required by Section 313 of SARA [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of carbonyl fluoride emitted or released from their facility annually.

Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Carbonyl fluoride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U033. This substance has been banned from land disposal and may be treated by incineration. Carbonyl fluoride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of carbonyl fluoride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, boots, aprons, and gauntlets) should be worn to prevent any skin contact with carbonyl fluoride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing

materials to carbonyl fluoride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to carbonyl fluoride.

Safety glasses, goggles, or face shields should be worn during operations in which carbonyl fluoride might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with carbonyl fluoride. Contact lenses should not be worn if the potential exists for carbonyl fluoride exposure.

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Sittig M [1985]. Handbook of toxic and hazardous chemicals. 2nd ed. Park Ridge, NJ: Noyes Publications.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CATECHOL

INTRODUCTION

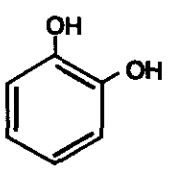
This guideline summarizes pertinent information about catechol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_6H_4(OH)_2$

- **Structure**



- **Synonyms**

  1,2-Benzenediol; pyrocatechol; o-dihydroxybenzene; pyrocatechin; o-diphenol; Durafur Developer C; o-hydroquinone; o-hydroxyphenol; oxyphenic acid; Pelagol Grey C; o-phenylenediol; pyrocatechinic acid

- **Identifiers**

  1. CAS No.: 120-80-9
  2. RTECS No.: UX1050000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Catechol is a colorless, crystalline solid that has a faint odor and sublimes easily.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 110.11
  2. Boiling point (760 mm Hg): 245.5°C (473.9°F)
  3. Specific gravity (water = 1): 1.344 at 40°C (104°F)
  4. Vapor density (air = 1 at boiling point of catechol): 3.79
  5. Melting point: 105°C (221°F)
  6. Vapor pressure at 118°C (244°F): 10 mm Hg
  7. Solubility: Soluble in water, ether, alcohol, hot benzene, and chloroform; very soluble in pyridine and acetone

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8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, flame, light, or air

2. Incompatibilities: Contact of catechol with strong oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released in a fire involving catechol.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to catechol; other sources rate catechol's fire hazard as slight.

1. Flash point: 127.2°C (261°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use water, dry chemical, or carbon dioxide to fight fires involving catechol.

Fires involving catechol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving catechol.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for catechol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (20 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned catechol a threshold limit value (TLV) of 5 ppm (20 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of skin and respiratory tract irritation and central nervous system effects associated with exposure to catechol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to catechol can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Catechol is a potential corrosive to the eyes, nose, upper respiratory tract, and skin. Aqueous solutions of up to 55% (0.05 M) were not injurious when instilled into rabbits' eyes [Grant 1986]. Application of 100 mg of dry catechol onto rabbits' eyes caused erythematous and edematous conjunctiva, moderate exudate, and corneal opacities (Draize score 103/110) within 24 hr. The 72-hr evaluation revealed severe conjunctivitis, iritis, and diffuse corneal opacities (Draize score 78/110). On the 14th day, corneal vascularization, granulation, and conical protrusion were observed [Flickinger 1976]. Administration of catechol onto rabbit skin produced moderate erythema and slight edema of the intact sites while necrosis occurred at the abraded areas. Catechol was thereby classified as a primary irritant (Draize score 5.5/8.0) [Flickinger 1976]. The dermal LD_{50} in the rabbit is 800 mg/kg [NIOSH 1992b]. Rats tolerated an 8-hr inhalation exposure to 1,500 mg/m^3 catechol without visible effects, but exposure to 2,000 or 2,800 mg/m^3 caused tremors after 6 to 7 hr. The tremors disappeared following the first experimental day. In addition, the 2,000- and 2,800-mg/m^3

concentrations caused the animals to develop irritated and blackened extremities and tails. Two of six rats exposed to 2,000 mg/m^3 developed blackened tails of which the terminal one inch was lost (undefined). Six out of six rats exposed to 2,800 mg/m^3 had both blackened tails and toes. All lost the terminal inch of their tails, while several had missing toes. The author concluded that severe exposure could lead to necrosis and sloughing of peripheral tissues [Flickinger 1976]. Lethal oral doses have induced hyperemia of the stomach and intestines of rats [Clayton and Clayton 1981]. The lowest reported oral LD_{50}s for the rat and mouse are 260 and 260 mg/kg, respectively [NIOSH 1992b]. Large doses (amounts not specified) of catechol can cause depression of the central nervous system, a prolonged rise in blood pressure, and degenerative changes in the renal tubules. Deaths from lethal doses or exposures in animals are caused from respiratory failure [Clayton and Clayton 1981; ACGIH 1991]. Rabbits that received repeated sublethal oral doses (200 mg/kg) had altered sleep times, leukopenia, anemia, and methemoglobinemia [Clayton and Clayton 1981; NIOSH 1992b]. An in vitro micromass teratogen test confirmed that catechol inhibits cell differentiation of rat embryo midbrain and limb cells [Flint and Maclean 1988]. Conversely, in an in vivo Chernoff/Kavlock assay, rats received one oral dose of 333, 667, or 1,000 mg catechol/kg on day 11 of pregnancy. The lethality rates in dams were 1/15, 5/15, and 10/15, respectively. The two upper levels caused a statistically significant dose-related decrease in litter size and an increase in perinatal loss. The 333-, 667-, and 1,000-mg/kg dose levels induced a 23.1%, 66.7%, and 80% incidence of hind limb tetany and paralysis, short or kinky tails, and urogenital malformations in the pups, respectively [Kavlock 1990]. Catechol is mutagenic in bacterial and mammalian test systems [NIOSH 1992b]. Groups of 50 Swiss mice received 5 g benzo(a)pyrene [B(a)P] with or without 2-mg catechol in acetone, three times per week for 52 weeks. Catechol plus B(a)P significantly increased the number of squamous cell carcinomas of the skin (31) when compared to benzo(a)pyrene alone (10), acetone controls (0), or negative controls (0). The rate of skin papillomas per affected mouse was also tripled when catechol plus B(a)P were administered. Catechol alone was not investigated in this study [IARC 1977]. When 2-mg catechol were suspended in 10-mg cholesterol pellets and implanted into the urinary bladders of mice for 25 weeks, a significant increase ($p=0.03$) in undefined carcinomas was induced above the control incidence [IARC 1977]. IARC found no adequate human studies and inadequate evidence of carcinogenic potential for the above animal studies. They classified it as a Group 3 chemical: The agent is not classifiable as to its carcinogenicity to humans [IARC 1977].

2. *Effects on Humans:* In humans, catechol is an eye and skin irritant, a skin sensitizer, and a depressant of the central nervous system. Catechol also causes eye burns that are slow to heal [Grant 1986]. Contact of catechol with the skin causes an eczematous dermatitis in sensitized workers. Absorption through the skin has resulted in signs and symptoms of illness resembling those of phenol poisoning, except that catechol-induced convulsions are more severe than those caused by phenol poisoning [ACGIH 1991]. Catechol is mutagenic in human test systems [NIOSH 1992b].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to catechol can cause redness, pain, and tearing of the eyes, runny nose, scratchy throat, and difficult breathing. Contact of catechol with the eyes may cause burns and permanent impairment of vision. Severe overexposure may cause convulsions.

2. *Chronic exposure:* Continued low-level exposure to catechol can cause eczematous dermatitis, with red, raised, and oozing areas of the skin.

- **Emergency Procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* If particulates, mists, or vapors of catechol are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if catechol or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve catechol and result in worker exposures to this substance:

—Use as an intermediate in the manufacture of 4-tertiary-butyl-catechol and certain chlorinated dibenzo-para-dioxins

—Use as a constituent of polymerization inhibitors and antioxidants

—Use in electro-sensitive copying papers, in photography, and in rubber compounding

—Use as a photographic developer, as an oxidation base in hair dye preparations, and as an analytical reagent

—Use as an antiseptic

—Use in the manufacture of specialty inks and light stabilizers

The following methods are effective in controlling worker exposures to catechol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to catechol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to catechol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of allergies and other findings consistent with diseases of the respiratory system or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to catechol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of catechol on the respiratory system and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although catechol can be measured in the urine of exposed individuals, no correlation between urinary and airborne catechol concentrations has yet been established. Therefore, no biological monitoring test acceptable for routine use is available for catechol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne catechol is determined by using an XAD-7 tube (100/50-mg sections, 15/50 mesh). Samples are collected at a recommended flow rate of 0.1 liter/min until a recommended air volume of 24 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If catechol contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with catechol should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of catechol, particularly its potential to cause eye and skin burns on contact.

A worker who handles catechol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where catechol or a solution containing catechol is handled, processed, or stored.

STORAGE

Catechol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of catechol should be protected from physical damage and should be stored separately from strong oxidizers, light, heat, sparks, and open flame. Because containers that formerly contained catechol may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving catechol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill.
5. Avoid raising dust during cleanup.
6. Sweep or vacuum the spilled material and gently place into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Catechol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of catechol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or otherwise use 10,000 lb or more of catechol per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of catechol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although catechol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this

substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of catechol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with catechol. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to catechol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to catechol.

If catechol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which catechol might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with catechol. Contact lenses should not be worn if the potential exists for catechol exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CELLULOSE

INTRODUCTION

This guideline summarizes pertinent information about cellulose for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $(C_6H_{10}O_5)_n$

- **Synonyms**

  Abicel; β-Amylose; Avicel; α-Cellulose; Cellex MX; Arbocel; Cupricellulose; Cellulose 248; Hydroxycellulose; Pyrocellulose; Sulfite cellulose

- **Identifiers**

  1. CAS No.: 9004-34-6
  2. RTECS No.: FJ5691460
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Cellulose is the principal fiber cell wall material of green terrestrial and marine plants; it is the most abundant polysaccharide produced in nature. Cellulose is a white substance that is odorless and tasteless. Natural cellulose exists both in microcrystalline and nonfibrous forms.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 300,000 to greater than 1,000,000 depending on the degree of polymerization of the particular cellulose
  2. Boiling point: Not applicable
  3. Specific gravity (water = 1): 1.27 to 1.61
  4. Vapor density: Not applicable
  5. Melting point: 260° to 270°C (500° to 518°F) (decomposes)
  6. Vapor pressure: Not applicable
  7. Solubility: Insoluble in water and organic solvents; dissolved by concentrated zinc chloride solutions, by ammoniacal copper hydroxide solutions, and by caustic alkali with carbon disulfide
  8. Evaporation rate: Not applicable

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Reactivity

1. Conditions contributing to instability: Heat or moisture

2. Incompatibilities: Contact of cellulose with water, bromine pentafluoride, sodium nitrate, or fluorine may cause fires and violent explosions.

3. Hazardous decomposition products: Toxic gases and particulates (such as carbon monoxide and carbon dioxide) may be released in a fire involving cellulose.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to cellulose; however, cellulose is combustible and may be flammable under certain conditions.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use water to fight fires involving cellulose.

Fires involving cellulose should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cellulose.

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cellulose is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cellulose (total dust) a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of local irritant effects associated with exposure to cellulose.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cellulose can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* There are no acute or chronic toxicity studies in animals for cellulose.

2. *Effects on Humans:* Like all dusts, cellulose dust produces mechanical irritation of the eyes, skin, or mucous membranes if it contacts these tissues in excessive amounts; there are no reports of other exposure-related effects of cellulose in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to cellulose, other than those of local irritation, have been reported.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to cellulose have been reported.

- **Emergency procedures**

WARNING

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of cellulose is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cellulose and may result in worker exposures to this substance:

—Manufacture of paper, fillers, cellophane, and rayon in the textile and paper industries

—Production of chemical derivatives such as certain explosives

—Use as a source of ethanol (enzymatic hydrolysis) and methanol (destructive distillation of wood)

—Use in the food industry to produce stabilizers, thickeners, and texturizers and in fillings and meringue

—Generated during wood processing and logging

The following methods are effective in controlling worker exposures to cellulose, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or

other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cellulose, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cellulose at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cellulose exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cellulose on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cellulose.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cellulose (total dust) is determined by using a tared, low-ash polyvinyl chloride (LAPVC) filter (5 microns). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by the gravimetric (weighing) method. This method has a sampling and analytical error of 0.10 and is described in the OSHA Computerized Information System [OSHA 1989], the *OSHA Chemical Information Manual* [OSHA 1987], and in NIOSH Method No. 0500 in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

A worker's exposure to airborne cellulose (respirable fraction) is determined by using a tared, low-ash polyvinyl chloride (LAPVC) filter (5 microns) preceded by a 10-mm nylon cyclone. Samples are collected at a maximum flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by the gravimetric (weighing) method. This method has a sampling and analytical error of 0.10 and is described in the OSHA Computerized Information System, the *OSHA Chemical Information Manual*, and in NIOSH Method No. 0600 in the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If a large amount of cellulose dust collects on the skin, workers should wash the affected areas with soap and water.

Clothing excessively contaminated with cellulose should be removed to avoid local irritation of the skin.

A worker who handles cellulose should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cellulose is handled, processed, or stored.

STORAGE

Cellulose should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of cellulose should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS

In the event of a spill involving cellulose, the following steps should be undertaken: use a clean shovel and place the material into a clean, dry container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cellulose is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cellulose; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cellulose emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cellulose is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cellulose exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the

requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent repeated or prolonged contact of the skin with cellulose dust. Safety glasses, goggles, or face shields should be worn during operations in which cellulose might contact the eyes (e.g., through dust particles).

REFERENCES CITED

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NIOSH [1984b]. Nuisance dust, respirable: Method 0600. In: Eller PM, ed. NIOSH manual of analytical methods. 3rd rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CESIUM HYDROXIDE

INTRODUCTION

This guideline summarizes pertinent information about cesium hydroxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CsOH

- **Synonyms**

  Cesium hydrate; cesium hydroxide dimer; cesium hydroxide, solid; cesium hydroxide, solution

- **Identifiers**

  1. CAS No.: 21351-79-1
  2. RTECS No.: FK9800000
  3. DOT UN: 2682 60 (solid); 2681 60 (solution)
  4. DOT label: Corrosive

- **Appearance and odor**

  Cesium hydroxide is a noncombustible, colorless or yellowish, deliquescent, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 149.92
  2. Boiling point: Data not available
  3. Specific gravity (water = 1): 3.68
  4. Vapor density: Data not available
  5. Melting point: 272.3°C (522.1°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Very soluble in water (generates heat); soluble in alcohol
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Cesium hydroxide is a strong base; in contact with water or moisture, it causes the generation of considerable heat.
  2. Incompatibilities: Contact of cesium hydroxide with

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

acids, many organic compounds, many metals (such as aluminum, lead, tin, or zinc), glass, oxygen, or carbon dioxide causes a violent reaction.

3. Hazardous decomposition products: None reported

4. Special precautions: Cesium hydroxide must be stored in silver or platinum and out of contact with air because of its reactivity with glass and carbon dioxide.

Flammability

The National Fire Protection Association has not assigned a flammability rating for cesium hydroxide; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to extinguish fires involving cesium hydroxide.

Fires involving cesium hydroxide should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of cesium hydroxide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cesium hydroxide. Structural firefighters' protective clothing may provide limited protection against fires involving cesium hydroxide.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cesium hydroxide [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cesium hydroxide a threshold limit value (TLV) of 2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of eye irritation associated with exposure to cesium hydroxide.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cesium hydroxide can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cesium hydroxide is irritating and corrosive to the eyes, mucous membranes, skin, and upper respiratory tract; the severity of these effects depends on the concentration of cesium hydroxide. Application of 5 mg cesium hydroxide to the eye of rabbits for 5 min, followed by rinsing with water, caused severe eye irritation; application of 5 mg to the skin of rabbits for 24 hr caused mild skin irritation [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50} for cesium hydroxide in the rat is 570 mg/kg, and the intraperitoneal LD_{50} in the same species is 100 mg/kg [NIOSH 1993]. The oral LD_{50} in mice is 800 mg/kg [NIOSH 1993; Sax and Lewis 1989; ACGIH 1991].

2. *Effects on Humans:* In humans, cesium hydroxide is irritating and corrosive to the eyes, nose, throat, and skin. Solutions containing 5% cesium hydroxide are regarded as safe for human skin contact; however, in contact with the eyes, a solution of this concentration causes extreme irritation and corneal corrosion [Sittig

1985]. Stronger solutions of cesium hydroxide cause eye and skin burns and may cause permanent damage. There is no other toxicological information on the effects of exposure to cesium hydroxide in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute inhalation exposure to cesium hydroxide include a burning sensation in nose, throat, and upper respiratory tract; runny nose; pain, redness and tearing of the eyes; difficult breathing; and redness, pain, and burns of the skin.

2. *Chronic exposure:* No signs or symptoms of continued low-level exposure to cesium hydroxide have been reported.

- **Emergency procedures**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately*** but ***gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cesium hydroxide or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

   NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following uses may involve cesium hydroxide and may result in worker exposures to this substance:

—Use as an electrolyte in alkaline storage batteries at subzero temperatures

—Use as a polymerization catalyst for siloxanes

—Use as an agent in the removal of sulfur from heavy oils

—Use as a raw material in the production of cesium salts, which are then used to produce cesium metal for electronic devices

The following methods are effective in controlling worker

exposures to cesium hydroxide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cesium hydroxide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cesium hydroxide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cesium hydroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cesium hydroxide on the eyes, skin, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitor-

ing test acceptable for routine use has yet been developed for cesium hydroxide.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cesium hydroxide is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. Elemental cesium analysis is conducted by atomic absorption spectroscopy, and the results are reported as cesium hydroxide. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cesium hydroxide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cesium hydroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cesium hydroxide, particularly its potential to cause eye and skin burns.

A worker who handles cesium hydroxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cesium hydroxide or a solution containing cesium hydroxide is handled, processed, or stored.

STORAGE

Cesium hydroxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Cesium hydroxide should not be stored in glass containers. Containers of cesium hydroxide should be protected from physical damage and should be stored separately from acids, organic compounds, metals, oxygen, carbon dioxide, moisture, heat, sparks, and open flame. Because containers that formerly contained cesium hydroxide may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cesium hydroxide or a solution containing cesium hydroxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Do not use water in clean-up.
4. For small dry spills, use a scoop or clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
5. For liquid spills, dilute the concentration of cesium hydroxide with water, neutralize the spilled material with dilute acid, absorb with sand or other noncombustible absorbent material, and place into closed containers for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

Emergency planning requirements

Cesium hydroxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

Reportable quantity requirements for hazardous releases

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cesium hydroxide; there is no reportable quantity for this substance.

Community right-to-know requirements

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cesium hydroxide emitted or released from their facility annually.

Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cesium hydroxide is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. D002. This substance has been banned from land disposal and may be treated by deactivation.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cesium hydroxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cesium hydroxide. Rubber gloves, rubber aprons, or protective suits and rubber boots should be worn when needed to prevent contact with cesium hydroxide. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under

actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cesium hydroxide permeation; however, neoprene and polyvinyl-chloride have been tested against chemically similar materials (sodium hydroxide and potassium hydroxide) and may provide greater than 8-hr of resistance to permeation. Since specific test data are not available for cesium hydroxide, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cesium hydroxide.

If cesium hydroxide is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cesium hydroxide might contact the eyes (e.g., through splashes of solutions containing cesium hydroxide). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cesium hydroxide. Contact lenses should not be worn if the potential exists for cesium hydroxide exposure.

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Occupational Health Guideline for Chlordane*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_6Cl_8$ (approx.)
- Synonyms: 1,2,4,5,6,7,8,8-Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane; 1,2,4,5,6,7,8,8-octachloro-2,3, 3a,4,7,7a-hexahydro-4,7-methanoindene
- Appearance and odor: Thick amber liquid with a characteristic chlorine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlordane is 0.5 milligram of chlordane per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlordane can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Exposure to chlordane may cause shaking, blurred vision, irritability, confusion, delirium, staggering, convulsions, and death. Swallowing chlordane may also cause nausea, vomiting, and diarrhea. Chlordane exposure may cause kidney and liver damage. Absorption of chlordane through the skin is rapid and has resulted in death.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlordane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlordane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders would be expected to be at increased risk from exposure. Examination of the nervous system, eyes, lungs, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to chlordane, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Chlordane predominantly affects the central nervous system, causing irritability, tremors, and convulsions. Chronic effects are reported in animals. Repeated oral administration to rabbits indicated a cumulative action at daily doses above 5 mg/kg; autopsy revealed focal necrosis of the liver, degenerative changes in the proximal convoluted tubules, pulmonary exudates and gastrointestinal irritation. In humans, inhalation and skin absorption have resulted in blurred vision, cough, confusion, ataxia, and delirium; ingestion has caused abdominal pain, nausea, vomiting, and diarrhea; severe intoxication has caused irritability, tremor, convulsions, and death. A suicidal person who ingested 6 g (104 mg/kg) of chlordane in talc suffered burns of the mouth, severe gastritis, diffuse pneumonia, anuria, mania, and convulsions; death occurred after 9.5 days; autopsy findings were severe necrotizing bronchopneumonia

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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and degeneration of renal tubule epithelium. Skin absorption of chlordane is rapid; a worker who spilled a 25% suspension of chlordane on clothing, which was not removed, began having convulsions 40 minutes later and died shortly thereafter. Technical-grade chlordane is stated to be irritating to the skin and mucous membranes, but this may be due to the presence of unreacted chemical intermediates.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 409.8 (approx).
2. Boiling point (760 mm Hg): (Decomposes); 175 C (347 F) (at 2 mm Hg)
3. Specific gravity (water = 1): 1.57– 1.67
4. Vapor density (air = 1 at boiling point of chlordane): 14
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 0.00001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 200 C (392 F) cause decomposition with formation of chlorine and hydrogen chloride gases.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, phosgene, and carbon monoxide) may be released when chlordane decomposes.
4. Special precautions: Chlordane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Since chlordane has such a low vapor pressure, warning properties are not considered. Grant describes certain effects produced by chlordane on the eyes, but these effects were caused by systemic poisoning. They were not local effects. Chlordane is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for chlordane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with chlordane.
- If employees' clothing has had any possibility of being contaminated with chlordane, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with chlordane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlordane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlordane, the person performing the operation should be informed of chlordane's hazardous properties.
- Where there is any possibility of exposure of an employee's body to chlordane, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chlordane should be removed immediately and not reworn until the chlordane is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where chlor-

dane may contact the eyes.

SANITATION

• Skin that becomes contaminated with chlordane should be immediately washed or showered with soap or mild detergent and water to remove any chlordane.
• Workers subject to skin contact with chlordane should wash with soap or mild detergent and water any areas of the body which may have contacted chlordane at the end of each work day.
• Eating and smoking should not be permitted in areas where chlordane is handled, processed, or stored.
• Employees who handle chlordane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlordane may occur and control methods which may be effective in each case:

Operation	Controls
Application as an insecticide on pre-planting soil, fire ants, and harvester ants (banned by EPA in 1976)	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.
• **Eye Exposure**
If chlordane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.
• **Skin Exposure**
If chlordane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlordane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.
• **Breathing**
If a person breathes in large amounts of chlordane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
• **Swallowing**
When chlordane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.
• **Rescue**
Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
• If chlordane is spilled or leaked, the following steps should be taken:
1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.
• Waste disposal method:
Chlordane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR CHLORDANE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s), including pesticide respirators which meet the requirements of this class. A chin-style or front- or back-mounted pesticide gas mask. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode. A powered chemical cartridge respirator with an organic vapor cartridge and a high efficiency filter, including pesticide respirators which meet the requirements of this class.
Greater than 500 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlordane; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 500 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chlorinated Camphene*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_{10}Cl_8$ (average)
- Synonyms: Toxaphene
- Appearance and odor: Waxy, amber-colored solid with a mild, turpentine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorinated camphene is 0.5 milligram of chlorinated camphene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorinated camphene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin. It may enter the body through the skin.

- **Effects of overexposure**

Overexposure to chlorinated camphene may cause nausea, mental confusion, agitation, involuntary trembling, convulsions, and unconsciousness. Contact with chlorinated camphene solutions may cause irritation of the skin.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorinated camphene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorinated camphene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system and the skin should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Chlorinated camphene is primarily a strong stimulant to the central nervous system. Most fatal cases of poisoning have been due to accidental ingestion, resulting in convulsions, loss of consciousness, and respiratory failure. The minimal acute lethal oral dose for man is 2 to 7 g. Few cases of intoxication due to occcupational exposure have been reported. Two cases of pneumonitis in insecticide sprayers using chlorinated camphene in an emulsion containing kerosene and xylene have been reported, but the significance of this finding is questionable as it relates to the toxicity of chlorinated camphene exposure. In solution, the substance is absorbed through the skin and causes skin irritation. In man, a single dermal application of 46 grams, or daily application of 2.4 grams, is very dangerous. Animals given repeated oral doses show degenerative changes in the liver and kidneys. Chronic exposure results in the accumulation of the substance in the fatty tissues. It is metabolized in the liver and excreted in the urine, probably in a conjugated form. Laboratory testing has indicated that this substance causes cancer in laboratory animals.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 414 (average)
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.63
4. Vapor density (air = 1 at boiling point of chlorinated camphene): 14.3
5. Melting point: 70 to 95 C (158 to 203 F)
6. Vapor pressure at 20 C (68 F): 0.2 to 0.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0003
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, especially when in contact with iron.
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving chlorinated camphene.
4. Special precautions: Emulsifiable concentrates of chlorinated camphene in xylene may decompose with liberation of much heat if allowed to come in contact with iron or aluminum above 70 C (158 F).

- **Flammability**

1. Flash point: 135 C (275 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, carbon dioxide

- **Warning properties**

Chlorinated camphene is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of chlorinated camphene on a filter, followed by extraction with petroleum ether, and gas chromatographic analysis. An analytical method for chlorinated camphene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquids containing chlorinated camphene and to prevent repeated or prolonged skin contact with solid chlorinated camphene.
- If employees' clothing may have become contaminated with solid chlorinated camphene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with solid chlorinated camphene or liquids containing chlorinated camphene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlorinated camphene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorinated camphene, the person performing the operation should be informed of chlorinated camphene's hazardous properties.
- Where exposure of an employee's body to liquids containing chlorinated camphene may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with solid chlorinated camphene should be removed promptly and non-impervious clothing which becomes contaminated with liquids containing chlorinated camphene should be removed immediately and such clothing should not be reworn until the chlorinated camphene is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid

chlorinated camphene or liquids containing chlorinated camphene may contact the eyes.

SANITATION

- Skin that becomes contaminated with solid chlorinated camphene should be promptly washed or showered and skin that becomes contaminated with liquids containing chlorinated camphene should be immediately washed or showered with soap or mild detergent and water to remove any chlorinated camphene.
- Eating and smoking should not be permitted in areas where solid chlorinated camphene or liquids containing chlorinated camphene are handled, processed, or stored.
- Employees who handle solid chlorinated camphene or liquids containing chlorinated camphene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorinated camphene may occur and control methods which may be effective in each case:

Operation	Controls
Mixing and formulation of liquid, dust, powder, and granular insecticides	Personal protective equipment
Use in application of liquid, dust, powder, or granular insecticide formulations	Personal protective equipment
Manufacture and packaging of chlorinated camphene	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlorinated camphene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chlorinated camphene gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If liquids containing chlorinated camphene get on the skin, immediately wash the skin using soap or mild detergent. If liquids containing chlorinated camphene soak through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent.

- **Breathing**

If a person breathes in large amounts of chlorinated camphene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chlorinated camphene has been swallowed, get medical attention immediately. If the chlorinated camphene is dissolved in a petroleum-based material, do not make the exposed person vomit. If medical attention is not immediately available and the chlorinated camphene is a powder or in a water base, get the person to vomit by having him touch the back of the throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water). Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorinated camphene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, use a procedure similar to that for small quantities.

- Waste disposal methods:

Chlorinated camphene may be disposed of:

1. By making packages of chlorinated camphene in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving chlorinated camphene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with afterburner and scrubber (alkali).

ADDITIONAL INFORMATION

To find additional information on chlorinated camphene, look up chlorinated camphene in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR CHLORINATED CAMPHENE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Vapor Concentration	
5 mg/m³ or less	Any pesticide chemical cartridge respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	Any pesticide chemical cartridge respirator with a full facepiece. A chin-style or front- or back-mounted pesticide gas mask. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A powered air-purifying pesticide respirator. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorinated camphene; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 200 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chlorinated Diphenyl Oxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{12}H_4Cl_6O$
- Synonyms: Hexachlorodiphenyl oxide
- Appearance: Waxy solid or liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorinated diphenyl oxide is 0.5 milligram of chlorinated diphenyl oxide per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorinated diphenyl oxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Exposure to chlorinated diphenyl oxide may cause an acne-like skin eruption or irritation. It may also injure the liver, resulting in such effects as fatigue, dark urine, and yellow jaundice.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorinated diphenyl oxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorinated diphenyl oxide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Chlorinated diphenyl oxide may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Chlorinated diphenyl oxide vapor causes an acne-form dermatitis (chloracne). In laboratory animals, cumulative liver damage has resulted from repeated bodily intake and, in general, the toxicity increases with the degree of chlorination; in guinea pigs, a single oral dose of .05 to 0.1 g/kg of material containing 4 or more equivalents of chlorine resulted in death 30 days after administration. Limited experience with humans has shown that exposure to even small amounts of the higher chlorinated derivatives may result in appreciable acne-form dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 377
2. Boiling point (760 mm Hg): 230 to 260 C (446 to 500 F)
3. Specific gravity (water = 1): 1.60
4. Vapor density (air = 1 at boiling point of chlorinated diphenyl oxide): 13
5. Melting point: Data not available

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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6. Vapor pressure at 20 C (68 F): Less than 0.00006 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 0.1

8. Evaporation rate (butyl acetate = 1): Not available

• **Reactivity**

1. Conditions contributing to instability: Heat.

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving chlorinated diphenyl oxide.

4. Special precautions: None.

• **Flammability**

1. Flash point: None

2. Autoignition temperature: 627 C (1163 F)

3. Flammable limits in air, % by volume: Not available

4. Extinguishant: Carbon dioxide, dry chemical

• **Warning properties**

Since there are no quantitative data relating warning properties to air concentrations of chlorinated diphenyl oxide, this material is treated as a substance with poor warning properties. The concentration of chlorinated diphenyl oxide in saturated air at 20 C could result in a significant exposure relative to the permissible exposure. There is no available information which indicates that chlorinated diphenyl oxides produce eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of chlorinated diphenyl oxide on a filter with subsequent extraction with iso-octane and gas chromatographic analysis. An analytical method for chlorinated diphenyl oxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with chlorinated diphenyl oxide.

• If employees' clothing may have become contaminated with chlorinated diphenyl oxide, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with chlorinated diphenyl oxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlorinated diphenyl oxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorinated diphenyl oxide, the person performing the operation should be informed of chlorinated diphenyl oxide's hazardous properties.

• Non-impervious clothing which becomes contaminated with chlorinated diphenyl oxide should be removed promptly and not reworn until the chlorinated diphenyl oxide is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where chlorinated diphenyl oxide may contact the eyes.

SANITATION

• Workers subject to skin contact with chlorinated diphenyl oxide should wash with soap or mild detergent and water any areas of the body which may have contacted chlorinated diphenyl oxide at the end of each work day.

• Skin that becomes contaminated with chlorinated diphenyl oxide should be promptly washed or showered with soap or mild detergent and water to remove any chlorinated diphenyl oxide.

• Eating and smoking should not be permitted in areas where chlorinated diphenyl oxide is handled, processed, or stored.

• Employees who handle chlorinated diphenyl oxide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorinated diphenyl oxide may occur and control methods which may be effective in each case:

Operation	Controls
Use as intermediate in organic synthesis in manufacture of flame-inhibiting polymers; corrosion inhibitors, dry cleaning detergents, thermal lubricants, additives for soaps and lotions, manufacture of hydraulic fluids, pesticides, wood preservatives, and electric insulators (Literature review suggests that this compound is of little or no industrial significance).	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If chlorinated diphenyl oxide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If chlorinated diphenyl oxide gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid chlorinated diphenyl oxide or liquids containing chlorinated diphenyl oxide soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of chlorinated diphenyl oxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When chlorinated diphenyl oxide has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If chlorinated diphenyl oxide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in solid form, small quantities may be swept onto paper or other suitable material, placed in an appropriate container and burned in a safe place (such as a fume hood). Larger quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
4. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

Chlorinated diphenyl oxide may be disposed of:

1. If in the solid form, by making packages of chlorinated diphenyl oxide in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device, or by dissolving in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. If in the liquid form, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill, or by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on chlorinated diphenyl oxide, look up chlorinated diphenyl oxide in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR CHLORINATED DIPHENYL OXIDE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
5 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 5 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors, acid gases, and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Chlorine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Cl_2
- Synonyms: None
- Appearance and odor: Amber liquid or greenish-yellow gas with a characteristic irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorine is a ceiling level of 1 part of chlorine per million parts of air (ppm) averaged over a 15-minute period (*Federal Register*, Vol. 43, No. 237, pp. 57601-03, 8 December 1978). This may also be expressed as 3 milligrams of chlorine per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 0.5 ppm (1.5 mg/m^3) measured over a 15-minute period. The NIOSH Criteria Document for Chlorine should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorine can affect the body if it is inhaled, or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Chlorine gas may cause severe irritation of the eyes and respiratory tract with tearing, runny nose, sneezing, coughing, choking, and chest pain. Severe breathing difficulties may occur which may be delayed in onset. Pneumonia may result. Severe exposures may be fatal. In high concentrations chlorine may irritate the skin and cause sensations of burning and prickling, inflammation, and blister formation. Liquid chlorine may cause eye and skin burns on contact.

2. Long-term Exposure: Repeated or prolonged exposure to chlorine may cause corrosion of the teeth and skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorine at potentially hazardous levels:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, cardiac status, and teeth should be stressed. The skin should be examined for evidence of chronic disorders. Simple tests of olfactory ability should be carried out.

—14" x 17" chest roentgenogram: Chlorine causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chlorine is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The above medical examinations are to be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Chlorine gas is a severe irritant of the eyes, mucous membranes, and skin. The odor threshold for chlorine has been reported at various concentrations and appears to be between 0.02 and 0.2 ppm for most subjects. Nasal irritation and coughing occur at about 0.5 ppm. There is evidence that olfactory fatigue develops at these low concentrations and that some tolerance is built up in

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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chronic industrial exposures. An accidental exposure of humans to unmeasured but high concentrations for a brief period caused burning of the eyes with lacrimation, burning of the nose and mouth with rhinorrhea, cough, choking sensation and substernal pain. These symptoms were frequently accompanied by nausea, vomiting, headache, dizziness, and sometimes syncope. Of 33 of the victims who were hospitalized, all suffered tracheobronchitis, 23 progressed to pulmonary edema, and of those, 14 to pneumonitis. Respiratory distress and substernal pain generally subsided within the first 72 hours; cough increased in frequency and severity after 2 to 3 days and became productive of thick mucopurulent sputum; cough disappeared by the end of 14 days. Prolonged or repeated exposure to 5 ppm may cause respiratory complaints, corrosion of the teeth, and inflammation of the mucous membranes of the nose. It has been reported that chronic exposure may increase susceptibility to respiratory infections. In high concentrations, chlorine irritates the skin and causes sensations of burning and pricking, inflammation, and vesicle formation. Liquid chlorine causes eye and skin burns on contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 70.9
2. Boiling point (760 mm Hg): −34.1 C (−29.3 F)
3. Specific gravity (water = 1): 1.41 (liquid)
4. Vapor density (air = 1 at boiling point of chlorine): 2.5
5. Melting point: −101 C (−149 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.7
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to burst.
2. Incompatibilities: Contact with combustible substances (such as gasoline and petroleum products, turpentine, alcohols, acetylene, hydrogen, ammonia, and sulfur) and finely divided metals may cause fires and explosions.
3. Hazardous decomposition products: None.
4. Special precautions: Chlorine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but is a strong oxidizer.
2. Compressed gas cylinders containing chlorine should be stored in accordance with 29 CFR 1910.101.

- **Warning properties**

1. Odor Threshold: The odor threshold for chlorine has been reported by several authors to be 0.01 ppm (Summer, May, and Stern).
2. Eye Irritation Level: Grant states that "exposure to concentrations of chlorine gas as low as 3 to 6 ppm in air causes sensation of stinging and burning of the eyes of some individuals, with associated blepharospasm, redness, and watering, but on continued exposure sensitivity may decrease and signs and symptoms diminish."

The ILO states that eye irritation may occur at 1 to 3 ppm.

3. Other Information: Patty states that "exposures to low concentrations, 10 to 20 mg/m^3 or 3 to 6 ppm, cause a stinging or burning sensation in the eyes, nose and throat, and sometimes headache due to irritation of the accessory nasal sinuses. There may be redness and watering of the eyes, sneezing, coughing, and huskiness or loss of the voice. Bleeding of the nose may occur, and sputum from the pharynx and trachea may be blood-tinged. There is little or no chest pain other than the muscular soreness associated with excessive coughing."
4. Evaluation of Warning Properties: Through its odor, chlorine can be detected below the permissible exposure limit, and through its irritant effects, chlorine can be detected within several times of the permissible exposure limit. For the purposes of this guideline, therefore, chlorine is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chlorine. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chlorine may be used. An analytical method for chlorine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may

be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorine, and to prevent the skin from becoming frozen from contact with vessels containing liquid chlorine.
- Where there is any possibility of exposure of an employee's body to liquid chlorine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chlorine should be removed immediately and not reworn until the chlorine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid chlorine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid chlorine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with chlorine should be immediately washed or showered to remove any chlorine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorine may occur and control methods which may be effective in each case:

Operation	Controls
Use as chlorinating and oxidizing agent in organic synthesis, manufacture of solvents, automotive antifreeze and antiknock compounds, plastics, resins, elastomers, pesticides, refrigerants, bleaching, and inorganic chemicals	Process enclosure; local exhaust ventilation; personal protective equipment
Use as fluxing, purification, and extraction agent in metallurgy	Process enclosure; local exhaust ventilation
Use as bacteriostat, disinfectant, odor control, and demulsifier in treatment of water and sewage	Process enclosure; local exhaust ventilation
Use as a chlorinating agent in the rubber and coatings industry	Process enclosure; local exhaust ventilation
Use as bleaching agent, cleaning agent, and disinfectant in laundries, dishwashers, cleaning powders, cleaning dairy equipment, and bleaching cellulose	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid chlorine or high concentrations of chlorine gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid chlorine or high concentrations of chlorine gas get on the skin, immediately flush the contaminated skin with water. If liquid chlorine or high concentrations of chlorine gas penetrate through the clothing, remove the clothing and immediately flush the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If chlorine is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty through a reducing agent, such as sodium bisulfide and sodium bicarbonate.

• Waste disposal method:

Chlorine may be disposed of by allowing gas to disperse at a safe location.

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RESPIRATORY PROTECTION FOR CHLORINE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Gas Concentration	
25 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against chlorine.** A gas mask with a chin-style or a front- or back-mounted canister providing protection against chlorine.** Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 25 ppm*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any full-facepiece gas mask providing protection against chlorine.** Any escape self-contained breathing apparatus with a full facepiece.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Chlorine is a strong oxidizer and should not come in contact with oxidizable materials.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorine; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 25 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chlorine Dioxide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: ClO_2
- Synonyms: None
- Appearance and odor: Yellow-green to orange gas or liquid with a pungent, sharp odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorine dioxide is 0.1 part of chlorine dioxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.3 milligram of chlorine dioxide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorine dioxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Chlorine dioxide may cause irritation of the eyes, nose, throat, and lungs. It may produce coughing, wheezing, and severe breathing difficulties which may be delayed in onset.

2. Long-term Exposure: Repeated exposure to chlorine dioxide may cause chronic bronchitis.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorine dioxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorine dioxide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system and eyes should be stressed.

—14" x 17" chest roentgenogram: Chlorine dioxide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chlorine dioxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

- **Summary of toxicology**

Chlorine dioxide gas is a severe respiratory and eye irritant. Delayed deaths occurred in animals after exposure to 150 to 200 ppm for less than 1 hour. Rats repeatedly exposed to 10 ppm died after 10 to 13 days of exposure; there was nasal and ocular discharge and dyspnea; autopsy revealed purulent bronchitis. Exposure of a worker to 19 ppm for an unspecified time period was fatal. Repeated acute exposure of workers to undetermined concentrations is stated to have caused eye and throat irritation, nasal discharge, cough, wheezing, bronchitis, and delayed onset of pulmonary edema. Repeated exposure may cause chronic bronchitis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 67.5
2. Boiling point (760 mm Hg): 11 C (52 F)
3. Specific gravity (water = 1): 1.6 (Liquid at boiling point)
4. Vapor density (air = 1 at boiling point of chlorine dioxide): 2.3
5. Melting point: −59 C (-74 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.8 (commercial solutions)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 130 C (266 F) cause rapid decomposition of gas. It will detonate if heated rapidly to 100 C (212 F).
2. Incompatibilities: Contact with dust and other combustible materials such as organic matter and sulfur may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine gas) may be released when chlorine dioxide decomposes.
4. Special precautions: Chlorine dioxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Self-accelerating decomposition temperature: 130 C (266 F)
3. Explosive limits in air: Concentrations over 40 percent in air will sustain a decomposition wave set off by an electric spark. Gas is explosive at concentrations over 10 percent and can be ignited by almost any form of energy such as sunlight, heat, or sparks.
4. Extinguishant: None known

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for chlorine dioxide of 0.1 ppm.
2. Eye Irritation Level: Grant states that "chlorine dioxide is a reddish yellow, poisonous gas which is very irritating to the respiratory tract. Industrially, men exposed to low concentrations of the gas in air have been noted occasionally to suffer from irritation of the eyes and to see haloes about lights, but these effects have been minor compared to respiratory irritation. The corneas of workers seeing haloes have not been examined to determine whether epithelial edema is present and responsible for this symptom." The *Documentation of TLV's* notes that "Elkins stated that a concentration of chlorine dioxide (ClO_2) of 5 ppm was definitely irritating."
3. Evaluation of Warning Properties: Since the odor threshold of chlorine dioxide is at the permissible exposure limit, this substance could be treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for chlorine dioxide had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorine dioxide.
- Where there is any possibility of exposure of an employee's body to liquid chlorine dioxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chlorine dioxide and any clothing which becomes wet with liquid chlorine dioxide should be removed immediately and not reworn until the chlorine dioxide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any

possibility of liquid chlorine dioxide contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid chlorine dioxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with chlorine dioxide should be immediately washed or showered with soap or mild detergent and water to remove any chlorine dioxide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorine dioxide may occur and control methods which may be effective in each case:

Operation	Controls
Use as bleaching agent for wood pulp and paper and textiles	Process enclosure; local exhaust ventilation; personal protective equipment
Use in water treatment to remove tastes and odors by oxidation; use in bleaching fats and oils, and to improve product, and leather dressing	Process enclosure; local exhaust ventilation; personal protective equipment
Use as bleaching and maturing agent in flour for baking; use as bleaching, cleaning, and unhairing agent in leather manufacture	Process enclosure; local exhaust ventilation; personal protective equipment
Use in chemical synthesis as oxidizing agent; use in control of microorganisms in fruit and vegetable processing as oxidizing agent; and as bacteria and algae control in aquariums and packaged pharmaceuticals	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid chlorine dioxide or strong concentrations of chlorine dioxide vapor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid chlorine dioxide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid chlorine dioxide penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation or burns are present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of chlorine dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If liquid chlorine dioxide has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the chlorine dioxide. Do not induce vomiting. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If chlorine dioxide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, evacuate persons not wearing protective equipment from spill area. Allow chlorine dioxide to evaporate while providing all available ventilation.

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RESPIRATORY PROTECTION FOR CHLORINE DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
5 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) containing non-combustible sorbents and providing protection against chlorine dioxide. A gas mask with a chin-style or a front- or back-mounted canister containing non-combustible sorbents and providing protection against chlorine dioxide. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing non-combustible sorbents and providing protection against chlorine dioxide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Chlorine Trifluoride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: ClF_3
- Synonyms: None
- Appearance and odor: Greenish-yellow, almost colorless liquid or gas with a sweet, but irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorine trifluoride is a ceiling level of 0.1 part of chlorine trifluoride per million parts of air (ppm). This may also be expressed as 0.4 milligram of chlorine trifluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorine trifluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Effects on humans from exposure to chlorine trifluoride have not been reported. Animal experiments have shown that exposure to this chemical can cause severe irritation of the eyes and respiratory tract. Severe breathing difficulties have occurred. These difficulties may sometimes be delayed in onset. Severe burns of the eyes and skin have been produced in animals from contact with this chemical.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorine trifluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorine trifluoride at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed. The skin and eyes should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Chlorine trifluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chlorine trifluoride is a severe pulmonary irritant in animals. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

- **Summary of toxicology**

Chlorine trifluoride gas is an extremely severe irritant of the eyes, respiratory tract, and skin. The injury caused by chlorine trifluoride can be extremely severe and, in part, attributed to its hydrolysis products including chlorine, hydrogen fluoride, and chlorine dioxide. Exposure of rats to 800 ppm for 15 minutes was fatal, but nearly all survived when exposed for 13 minutes. There was severe inflammation of all exposed mucosal surfaces, resulting in lacrimation, corneal ulceration, and burning of exposed areas of skin. In another study, exposure of rats to 480 ppm for 40 minutes or to 96 ppm

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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for 3.7 hours was fatal; in the latter group, there were pulmonary edema and marked irritation of the bronchial mucosa. Effects in humans have not been reported, but exposure may cause some effects; inhalation may be expected to cause pulmonary edema, and contact with eyes or skin may cause severe burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 92.5
2. Boiling point (760 mm Hg): 11.8 C (53 F)
3. Specific gravity (water = 1): 1.88 (liquid)
4. Vapor density (air = 1 at boiling point of chlorine trifluoride): 3.14
5. Melting point: −76.3 C (-105 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): Violent reaction to form chlorine gas and hydrofluoric acid
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Chlorine trifluoride decomposes above 220 C (428 F) and may explode container.
2. Incompatibilities: Chlorine trifluoride will cause most combustible materials to ignite spontaneously. The exceptions are dry, highly fluorinated polymers such as "Teflon" and "Kel-F," the metals used in storage containers (monel, copper, and stainless steel) or gaskets (teflon), nitrogen gas or air, and the inert gases (neon, etc.). Chlorine trifluoride reacts violently with water, sand, silicon-containing compounds, glass, and asbestos.
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and hydrogen fluoride) may be released when chlorine trifluoride decomposes.
4. Special precautions: Chlorine trifluoride will attack all forms of plastics, rubber, and resins, except the higly fluorinated polymers "Teflon" and Kel-F."

- **Flammability**

1. Not combustible by itself, but is very reactive and may cause fire on contact with organic matter.

- **Warning properties**

Odor Threshold: Deichmann and Gerarde note that chlorine trifluoride has a "somewhat sweet odor." No quantitative information is available, however, concerning the odor threshold.

2. Irritation Level: Grant states that "chlorine trifluoride is an extremely reactive, corrosive and irritating gas which experimentally has been observed to cause a severe reaction in the lungs and in all exposed mucous membranes. It is highly irritating to the skin and eyes, and has caused severe corneal ulcers in dogs."
3. Evaluation of Warning Properties: Since no quantitative data are available relating warning properties to air concentrations of chlorine trifluoride, this gas is treated as a material with poor warning properties. In addition, since chlorine trifluoride is a powerful oxidizer, it should not be allowed to contact combustible materials.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chlorine trifluoride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

At the time of publication of this guideline, no measurement method for chlorine trifluoride had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorine trifluoride.
- Where there is any possibility of exposure of an employee's body to liquid chlorine trifluoride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes contaminated with chlorine trifluoride should be removed immediately and

not reworn until the chlorine trifluoride is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid chlorine trifluoride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid chlorine trifluoride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with chlorine trifluoride should be immediately washed or showered to remove any chlorine trifluoride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorine trifluoride may occur and control methods which may be effective in each case:

Operation	Controls
use as a fluorinating agent in organic and inorganic chemical synthesis; use in the separation of uranium isomers	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a cutting agent for well castings in oil well drilling	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a rocket fuel oxidizer as an igniter and propellant in liquid propellant engines; use as an incendiary	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid chlorine trifluoride or strong concentrations of chlorine trifluoride vapor get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid chlorine trifluoride or strong concentrations of chlorine trifluoride vapor get on the skin, immediately flush the contaminated skin with large quantities of water. If liquid chlorine trifluoride or strong concentrations of chlorine trifluoride vapor penetrate through the clothing, remove the clothing immediately and flush the skin with large amounts of water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of chlorine trifluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If liquid chlorine trifluoride has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the chlorine trifluoride. Do not induce vomiting. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If chlorine trifluoride is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in the liquid form, evacuate persons not wearing protective equipment from spill area. Allow chlorine trifluoride to evaporate while providing all available ventilation.

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RESPIRATORY PROTECTION FOR CHLORINE TRIFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A gas mask containing non-combustible sorbents and providing protection against chlorine trifluoride. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorine trifluoride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 20 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chloroacetaldehyde

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $ClCH_2CHO$
- Synonyms: 2-Chloroethanal; chloroacetaldehyde (40% aqueous)
- Appearance and odor: Colorless liquid with a very sharp, irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chloroacetaldehyde is a ceiling level of 1 part of chloroacetaldehyde per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3 milligrams of chloroacetaldehyde per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chloroacetaldehyde can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

Chloroacetaldehyde causes skin burns, irritation of the throat, nose, and lungs, and serious irritation of the eyes.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chloroacetaldehyde.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chloroacetaldehyde at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from chloroacetaldehyde exposure.

—Eye disease: Chloroacetaldehyde is a potent eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—Skin disease: Chloroacetaldehyde is a skin irritant and possibly a skin sensitizer. Those with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of chloroacetaldehyde might cause exacerbation of symptoms due to its irritant and potentially sensitizing properties.

—Kidney disease: Although chloroacetaldehyde is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although chloroacetaldehyde is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Overexposure to chloroacetaldehyde produces corrosive destruction and degradation of lipids and membrane structures, causing intense irritation and edema of the eyes, mucous membranes, respiratory tract, and skin. Prolonged exposure to the liquid causes tissue destruction, chemical burns, and residual scarring. Some permanent damage to the eye may occur. Chloroacetaldehyde and its metabolite, chloroacetic acid, are

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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excreted by the kidneys. The possibility of skin and respiratory sensitization should be considered.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 78.5
2. Boiling point (760 mm Hg): 85 C (185 F)
3. Specific gravity (water = 1): 1.19 for 40% aqueous solution
4. Vapor density (air = 1 at boiling point of chloroacetaldehyde): 2.7 for 40% aqueous solution
5. Melting point: −16.3 C (3 F) for 40% aqueous solution
6. Vapor pressure at 45 C (113 F): 100 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with oxidizing materials and acids may cause fires or explosions. The compound reacts with water to form a hydrate with the evolution of some heat.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving chloroacetaldehyde.
4. Special precautions: Chloroacetaldehyde forms a water-insoluble polymer in storage, especially in the presence of small amounts of acid.

- **Flammability**

1. Flash point: 88 C (190 F)(closed cup) for 40% aqueous solution
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam

- **Warning properties**

1. Odor Threshold: By analogy to crotonaldehyde and acetaldehyde, both of which the *Handbook of Organic Industrial Solvents* states have odor thresholds less than 1 ppm, the odor threshold of chloroacetaldehyde is assumed to be less than 1 ppm.
2. Irritation Levels: The *Documentation of TLV's* states that "chloroacetaldehyde presents a serious hazard from inhalation of its vapor, which is irritating to the eyes, nose, and throat . . . . This aldehyde is somewhat more irritating than formaldehyde."

According to Grant, formaldehyde causes "definite irritation of the eyes and lacrimation . . . at a concentration of 20 ppm in air. Even at concentrations from 0.5 to 0.005 ppm a sensation of eye irritation is detectable, and it (formaldehyde) can be sensed as low as 0.01 ppm by some people."

The *Documentation of TLV's*, in addition, states that a "threshold limit of 1 ppm (chloroacetaldehyde) is recommended to prevent irritative effects. Analogy with other aldehydes and practical experience suggest that the TLV will not prevent all complaints of irritation, and it should be used only with caution in continuous, repeated exposure situations."

3. Evaluation of Warning Properties: By analogy to other aldehydes, it is assumed that chloroacetaldehyde can be detected at the permissible exposure through its odor and irritant effects. For the purposes of this guideline, therefore, chloroacetaldehyde is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chloroacetaldehyde. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- Method

An analytical method for chloroacetaldehyde is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent any possibility of skin contact with chloroacetaldehyde at or above a concentration of 0.1%.

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing chloroacetaldehyde below a concentration of 0.1%.

• Clothing contaminated with chloroacetaldehyde should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chloroacetaldehyde from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chloroacetaldehyde, the person performing the operation should be informed of chloroacetaldehyde's hazardous properties.

• Where there is any possibility of exposure of an employee's body to solutions containing in excess of 0.1% chloroacetaldehyde, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with chloroacetaldehyde should be removed immediately and not reworn until the chloroacetaldehyde is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid chloroacetaldehyde contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid chloroacetaldehyde, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with chloroacetaldehyde should be immediately washed or showered to remove any chloroacetaldehyde.

• Employees who handle liquid chloroacetaldehyde should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chloroacetaldehyde may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture of 2-aminothiazole	Process enclosure; general dilution ventilation; personal protective equipment (with barrier creams)
Liberation during use in diethylacetal in acid media during chemical synthesis, such as p-aminothiazole	Process enclosure; general dilution ventilation; personal protective equipment
Use during control of algae, bacteria, and fungi in water	General dilution ventilation; personal protective equipment (with barrier creams)
Use as a spinning solution of poly B-alanine	General dilution ventilation; personal protective equipment (with barrier creams)
Liberation from intermediate steps in organic synthesis	Local exhaust ventilation
Use during debarking operations	Local exhaust ventilation; personal protective equipment
Use of diethylacetal in an acid media during chemical synthesis such as p-aminothiazole	Process enclosure; general dilution ventilation; personal protective equipment (with barrier creams)

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If chloroacetaldehyde gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible.

• **Skin Exposure**

If chloroacetaldehyde gets on the skin, immediately flush the contaminated skin with water. If chloroacetaldehyde soaks through the clothing, remove the clothing immediately and flush the skin with water. When there are chemical burns or evidence of skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of chloroacetaldehyde, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When chloroacetaldehyde has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If chloroacetaldehyde is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

Chloroacetaldehyde may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an effluent gas cleaning device.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Chloroacetaldehyde," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR CHLOROACETALDEHYDE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
50 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 250 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for alpha-Chloroacetophenone

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5COCH_2Cl$
- Synonyms: Phenyacyl chloride; omega=chloroacetophenone; chloroacetophenone; chloromethyl phenyl ketone; phenyl chloromethyl ketone; "tear gas"; CN
- Appearance and odor: Colorless to gray solid with a sharp, irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for alpha-chloroacetophenone is 0.05 part of alpha-chloroacetophenone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.3 milligram of alpha-chloroacetophenone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

alpha-Chloroacetophenone can cause irritation of the eyes and skin upon contact and irritation of the lungs if it is inhaled. It can also cause difficulty if it is swallowed.

- **Effects of overexposure**

alpha-Chloroacetophenone vapors may cause a tingling or runny nose, burning and/or pain of the eyes, blurred vision, and tears. Burning in the chest, difficult breathing, and nausea may occur. Skin irritation, rash, or burns may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to alpha-chloroacetophenone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to alpha-chloroacetophenone at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from alpha-chloroacetophenone exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of alpha-chloroacetophenone might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Skin disease: alpha-Chloroacetophenone is irritating to the skin, especially if moist. Persons with pre-existing skin diseases may be more susceptible to the effects of alpha-chloroacetophenone.

—Eye disease: alpha-Chloroacetophenone is a potent lacrimator and eye irritant and may cause corneal damage. Persons with pre-existing eye diseases may be at increased risk from exposure.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

alpha-Chloroacetophenone is a highly irritating substance. Exposure to low concentrations produces lacrimation and irritation of the eyes and upper respiratory tract. Exposure to high concentrations produces marked conjunctivitis and may cause corneal damage. Pulmonary edema may occur, often delayed for some 12 hours after exposure. No chronic effects are reported.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 155
  2. Boiling point (760 mm Hg): 247 C (477 F)
  3. Specific gravity (water = 1): 1.32
  4. Vapor density (air = 1 at boiling point of alpha-chloroacetophenone): 5.2
  5. Melting point: 59 C (138 F)
  6. Vapor pressure at 20 C (68 F): 0.012 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Very much less than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Water or steam
  3. Hazardous decomposition products: Toxic and corrosive vapors are produced when combined with steam or water.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 118 C (244 F)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Not applicable
  4. Extinguishant: Carbon dioxide or dry chemical
- **Warning properties**
  1. Odor Threshold: According to the *Documentation of TLV's*, the odor threshold is 0.1 mg/m^3.
  2. Irritation Levels: According to the *Documentation of TLV's*, "irritation thresholds range from 0.15 to 0.4 mg/m^3, lacrimation thresholds from 0.3 to 0.4 mg/m^3 . . ."
  3. Evaluation of Warning Properties: Through its odor and irritant effects, alpha-chloroacetophenone can be detected below the permissible exposure limit; therefore, it is considered to have adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for alpha-chloroacetophenone is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid alpha-chloroacetophenone or liquids containing alpha-chloroacetophenone.
- If employees' clothing may have become contaminated with solid alpha-chloroacetophenone, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with alpha-chloroacetophenone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of alpha-chloroacetophenone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the alpha-chloroacetophenone, the person performing the operation should be informed of alpha-chloroacetophenone's hazardous properties.
- Non-impervious clothing which becomes contaminated with alpha-chloroacetophenone should be removed immediately and not reworn until the alpha-chloroacetophenone is removed from the clothing.
- Where there is any possibility that employees' eyes may be exposed to alpha-chloroacetophenone, an eyewash fountain should be provided within the immediate work area for emergency use.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid alpha-chloroacetophenone or liquids containing alpha-chloroacetophenone contacting the eyes.

SANITATION

• Skin that becomes contaminated with alpha-chloroacetophenone should be immediately washed or showered with soap or mild detergent and water to remove any alpha-chloroacetophenone.

• Eating and smoking should not be permitted in areas where solid alpha-chloroacetophenone is handled, processed, or stored.

• Employees who handle solid alpha-chloroacetophenone or liquids containing alpha-chloroacetophenone should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to alpha-chloroacetophenone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during loading of solutions for aerosols for law enforcement and civilian protective devices	General dilution ventilation; respiratory protective equipment
Liberation during manufacture	Process enclosure; general dilution ventilation
Liberation during denaturing of industrial alcohol	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If alpha-chloroacetophenone gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If alpha-chloroacetophenone gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If alpha-chloroacetophenone soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. When there are chemical burns or evidence of skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of alpha-chloroacetophenone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When alpha-chloroacetophenone has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If alpha-chloroacetophenone is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

alpha-Chloroacetophenone may be disposed of:

1. By making packages of alpha-chloroacetophenone in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving alpha-chloroacetophenone in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "alpha-Chloroacetophenone," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• Rothberg, S.: "Skin Sensitization Potential of the Riot Control Agents," *Military Medicine*, 135:552-556, July 1970.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR ALPHA-CHLOROACETOPHENONE

Condition	Minimum Respiratory Protection* Required Above 0.05 ppm
Particulate and Vapor Concentration	
15 mg/m³ (2.5 ppm) or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s) and high efficiency particulate filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister with a high efficiency particulate filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ (16 ppm) or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 100 mg/m³ (16 ppm) or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask with a full facepiece providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROACETYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about chloroacetyl chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_2H_2Cl_2O$

- **Structure**

  $ClCH_2COCl$

- **Synonyms**

  Chloroacetic acid chloride; chloroacetic chloride; monochloroacetyl chloride; chloracetyl chloride

- Identifiers

  1. CAS No.: 79-04-9
  2. RTECS No.: AO6475000
  3. DOT UN: 1752 59
  4. DOT label: Corrosive

- **Appearance and odor**

  Chloroacetyl chloride is a colorless to slightly yellow liquid with a strong, pungent odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 112.94
  2. Boiling point (760 mm Hg): 105° to 110°C (221° to 230°F)
  3. Specific gravity (water = 1): 1.42 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chloroacetyl chloride): Data not available
  5. Melting point (at 760 mm Hg): 106°C (222.8°F)
  6. Freezing point: -22.5°C (-8.5°F)
  7. Vapor pressure at 21°C (69.8°F): 20 mm Hg
  8. Solubility: Insoluble in water; soluble in ether and acetone
  9. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, and water
  2. Incompatibilities: Contact of chloroacetyl chloride

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with water causes decomposition and the release of hydrogen chloride gas and chloroacetic acid; avoid contact with alcohols, amines, and alkalis.

3. Hazardous decomposition products: Toxic gases (such as hydrogen chloride, phosgene, and chlorine) may be released in a fire involving chloroacetyl chloride.

4. Special precautions: Keep chloroacetyl chloride away from moisture or water.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to chloroacetyl chloride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire. Do not use water.

Fires involving chloroacetyl chloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloracetyl chloride should be moved from the fire area if it is possible to do so safely. If this is not possible, cool fire-exposed containers from the sides with water until well after the fire is out. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloroacetyl chloride. Chemical protective clothing that is specifically recommended for chloroacetyl chloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chloroacetyl chloride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chloroacetyl chloride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.2 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloroacetyl chloride a threshold limit value (TLV) of 0.05 ppm (0.23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 0.15 ppm (0.69 mg/m^3) for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 minutes. The ACGIH has also assigned a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of skin and respiratory irritation associated with choloracetyl chloride exposure. The ACGIH limits are based on the risk of eye, skin, and respiratory irritation and systemic effects associated with exposure to chloroacetyl chloride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloroacetyl chloride can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Chloroacetyl chloride is highly corrosive to tissues; in animals it affects the lungs, eyes, and skin. In rabbits the dermal LD_{50} is 178 mg/kg and the dermal LD_{LO} ranges from 316 to 501 mg/kg [AIHA 1987; NIOSH 1989; ACGIH 1991]. The LC_{50} in the rat is 1,000 ppm for a 4-hr exposure [NIOSH 1989]. A 5 to 10 min exposure to a

concentration of 4 ppm caused respiratory difficulty in rats, but no effect was observed from the inhalation of a 2.5-ppm chloroacetyl chloride concentration for 7 hr [NLM 1992; AIHA 1987]. A 30-day inhalation study with rats, mice, and hamsters showed that these animals develop eye and respiratory irritation at an airborne concentration of 2.5 ppm [NLM 1992]. The oral LD_{50} in the rat is 120 mg/kg; cough and dermatitis were noted before death [NIOSH 1989].

2. *Effects on Humans:* In humans, chloroacetyl chloride is corrosive to the skin and eyes and affects the respiratory system [Sittig 1985]. The effects of acute workplace exposure include mild to moderate skin irritation and burns, lacrimation, mild eye burns, mild to moderate respiratory effects with cough, dyspnea, cyanosis, and mild gastrointestinal effects [ACGIH 1991; AIHA 1987]. Respiratory effects include coughing, difficult breathing, and oxygen insufficiency [ACGIH 1991a]. Workers exposed to peak chloroacetyl chloride concentrations of 140 ppb developed eye irritation and reported experiencing minimal respiratory irritation [NLM 1992]. In an industrial accident, a worker was drenched by a mixture containing chloroacetyl chloride, xylidine, benzene, and sodium carbonate. Although immediately put under a shower, he suffered extensive first- and second-degree burns, developed pulmonary edema, and had three episodes of cardiac arrest during emergency treatment. He went into a coma that lasted several weeks; the ultimate outcome of this case is not reported [ACGIH 1991; NLM 1992]. Workers involved in the rescue of this employee suffered blisters on their hands and complained of tightness of the chest and slight nausea for as long as 2 days after the incident [NLM 1992]. Most of the acute effects experienced by this worker are believed to have been caused by the chloroacetyl chloride.

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute inhalation overexposure to chloroacetyl chloride include pain, redness, and tearing of the eyes, sore throat, pain in the chest, fluid in the lungs, and difficult breathing. Contact with the liquid can cause severe skin or eye burns.

2. *Chronic exposure:* The signs and symptoms of continued low-level exposure to chloroacetyl chloride may include a burning sensation in the upper respiratory tract, wheezing, laryngitis, and shortness of breath.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of chloroacetyl chloride! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chloroacetyl chloride or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloroacetyl chloride and may result in worker exposures to this substance:

—Manufacture of herbicides (such as alachlor, allidochlor, butachlor, and others) and tear gas

—Use as an intermediate in the manufacture of chloroacetophenone and other chemicals

—Manufacture of pharmaceuticals, such as chlordiazepoxide hydrochloride, diazepam, lidocaine, and mianserin

The following methods are effective in controlling worker exposures to chloroacetyl chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Personal protective equipment and local ventilation are a necessity at chloroacetyl chloride transfer points where leakage can be expected.

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chloroacetyl chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloroacetyl chloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloroacetyl chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloroacetyl chloride on the respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloroacetyl chloride.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chloroacetyl chloride is determined by using a XAD-2 tube coated with 1- (2-pyridyl)piperazine. Samples are collected at a recommended flow rate of 0.05 liter/min until a recommended air volume of 10 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If chloroacetyl chloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with chloroacetyl chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chloroacetyl chloride, particularly its potential to cause eye and skin burns.

A worker who handles choloroacetyl chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chloroacetyl chloride or a solution containing chloroacetyl chloride is handled, processed, or stored.

STORAGE

Chloroacetyl chloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chloroacetyl chloride should be protected from physical damage and should be stored separately from water, steam, surface moisture, oxidizing agents, strong bases, alcohols, heat, sparks, and open flame. Because containers that formerly contained chloroacetyl chloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chloroacetyl chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the chloroacetyl chloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloroacetyl chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloroacetyl chloride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chloroacetyl chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chloroacetyl chloride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloroacetyl chloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of

an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with chloroacetyl chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chloroacetyl chloride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chloroacetyl chloride.

If chloroacetyl chloride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chloroacetyl chloride might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloroacetyl chloride.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROBENZENE

INTRODUCTION

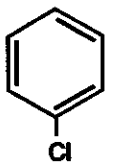
This guideline summarizes pertinent information about chlorobenzene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_6H_5Cl

- **Structure**



- **Synonyms**

  Monochlorobenzene, MCB, phenyl chloride, chlorobenzol, benzene chloride

- **Identifiers**

  1. CAS No.: 108-90-7
  2. RTECS No.: CZ0175000
  3. DOT UN: 1134 27
  4. DOT label: Flammable liquid

- **Appearance and odor**

  Chlorobenzene is a colorless to yellowish liquid with a mild, aromatic, almond-like odor. The odor threshold of chlorobenzene is 0.21 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 112.6
  2. Boiling point (760 mm Hg): 131° to 132°C (267.8° to 270°F)
  3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chlorobenzene): 3.9
  5. Melting point: -45°C (-49°F)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

6. Vapor pressure at 20°C (68°F): 8.8 mm Hg

7. Solubility: Insoluble in water; soluble in alcohol, benzene, chloroform, and ether

8. Evaporation rate (ether = 1): 8.2

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of chlorobenzene with strong oxidizers, dimethyl sulfoxide, powdered sodium, phosphorus trichloride and sodium, or silver perchlorate causes fire, explosion, or a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving chlorobenzene.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to chlorobenzene.

1. Flash point: 27.8°C (82°F)

2. Autoignition temperature: 593°C (1,099°F)

3. Flammable limits in air (% by volume): Lower, 1.3; upper, 9.6

4. Extinguishant: Use carbon dioxide, dry chemical, water spray, or standard foam to fight fires involving chlorobenzene.

Fires involving chlorobenzene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of chlorobenzene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorobenzene. Structural firefighters' protective clothing may provide limited protection against fires involving chlorobenzene.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chlorobenzene is 75 ppm (350 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for chlorobenzene [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorobenzene a threshold limit value (TLV) of 10 ppm (46 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of liver and other effects associated with exposure to chlorobenzene [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorobenzene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to chlorobenzene causes irritation, narcosis, and liver and kidney damage. In contact with the eyes of rabbits or skin of guinea pigs, chlorobenzene caused a moderate degree of irritation [ACGIH 1991]. Rats, rabbits, and guinea pigs exposed to chlorobenzene at a concentration of 1,000 ppm for 7 hr/day, 5 days/week for 44 days showed signs of lung, liver, and kidney damage; however, exposure to a 475-ppm concentration on the same regimen caused only slight liver damage in one species [Hathaway et al. 1991; ACGIH 1991]. Cats exposed to an 8,000-ppm concentration of chlorobenzene for 30 min showed signs of severe narcosis and died 2 hr after cessation of exposure; however, cats survived exposure to a 660-ppm concentration for 1 hr [Hathaway et al. 1991]. Acutely poisoned animals showed signs of eye and nose irritation and narcosis [Hathaway et al. 1991]. The oral LD_{50} in rats is 2,290 mg/kg, and the lowest lethal concentration in mice is 15 g/m^3 [NIOSH 1993]. In gavage studies of rats and mice administered chlorobenzene 5 days/week for 91 days, dose-dependent necrosis of the liver, degeneration or focal necrosis of the proximal tubules of the kidney, and myeloid or lymphoid depletion of the spleen, bone marrow, and thymus were seen at doses of 250 mg/kg/day or greater in both sexes [Hathaway et al. 1991]. In 2-year gavage studies of male and female rats and mice, male rats administered chlorobenzene doses of 120 mg/kg had a slight but statistically significant increase in neoplastic nodules of the liver. No increase in the incidence of liver tumors was seen in the mice or the female rats [Hathaway et al. 1991].

2. *Effects on Humans:* Exposure to chlorobenzene at a concentration of 200 ppm causes eye and nose irritation, and exposure to higher concentrations causes central nervous system depression. In contact with the skin for brief exposures, liquid chlorobenzene causes only mild irritation; however, prolonged or repeated contact can lead to burns of the skin [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to chlorobenzene may cause redness and inflammation of the eyes and eyelids, runny nose, sore throat, redness and irritation of the skin, headache, dizziness, drowsiness, incoherence, ataxia, loss of consciousness, twitching of the extremities, deep and rapid respiration, and irregular heartbeat. Respiratory arrest may follow.

2. *Chronic exposure:* Long-term exposure to chlorobenzene may cause chronic central nervous system depression: headache, dizziness, and somnolence. Based on effects seen in animals, chronic exposure may cause elevated liver enzymes, enlarged and tender liver, and blood, pus, or protein in the urine. Prolonged or repeated skin contact may cause skin burns.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of chlorobenzene. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chlorobenzene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorobenzene and may result in worker exposures to this substance:

—Use as a solvent for paints, adhesives, polishes, waxes, and natural rubber, and as a solvent carrier for methylene diisocyanate

—Use as a dry-cleaning agent

—Manufacture of phenol, o- and p-chloronitrobenzene, aniline, DDT, and pharmaceuticals

The following methods are effective in controlling worker exposures to chlorobenzene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chlorobenzene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, central nervous system, liver, eyes, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is

exposed to chlorobenzene at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory or central nervous system, liver, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorobenzene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorobenzene on the respiratory or central nervous system, liver, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Although chlorobenzene or its metabolites can be detected in the blood or adipose tissue of exposed individuals, no biological monitoring test acceptable for routine use has yet been developed for chlorobenzene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorobenzene is determined by using a coconut shell solid sorbent tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 40 liters is collected. The samples are then desorbed with carbon disulfide to extract the chlorobenzene. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg/sample. This method is described in NIOSH Method No. 1003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If chlorobenzene contacts the skin, workers should flush the affected areas immediately with plenty of water, followed by washing with soap and water.

Clothing contaminated with chlorobenzene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chlorobenzene, particularly its potential to be irritating to the eyes and skin.

A worker who handles chlorobenzene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorobenzene or a solution containing chlorobenzene is handled, processed, or stored.

STORAGE

Chlorobenzene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of chlorobenzene should be protected from physical damage and should be stored separately from oxidizers, dimethyl sulfoxide, silver perchlorate, other incompatible chemicals, heat, sparks, and open flame. Only nonsparking tools may be used to handle chlorobenzene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained chlorobenzene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorobenzene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small dry spills, use a clean, nonsparking shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
7. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the chlorobenzene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Chlorobenzene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for chlorobenzene is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more of chlorobenzene per calendar year or otherwise use 10,000 lb or more of chlorobenzene per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorobenzene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Chlorobenzene is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U037. It is approved for land disposal as long as the concentration of chlorobenzene in the waste or treatment residual does not exceed 5.7 mg/kg. Chlorobenzene also may be disposed of in an

organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorobenzene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent skin contact with chlorobenzene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material have demonstrated greater than 8 hr of resistance to breakthrough under continuous contact: Viton, Barricade, and Responder. Polyvinyl-alcohol and Teflon have shown resistance to breakthrough between 4 and 8 hr.

If chlorobenzene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chlorobenzene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chlorobenzene. Contact lenses should not be worn if the potential exists for chlorobenzene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROBENZYLIDENE MALONONITRILE

INTRODUCTION

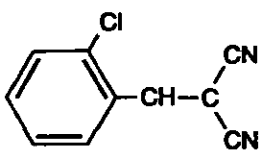
This guideline summarizes pertinent information about o-chlorobenzylidene malononitrile for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{10}H_5ClN_2$

- **Structure**



- **Synonyms**

CS; OCBM; (o-chlorobenzal)malononitrile; beta,beta-dicyano-o-chlorostyrene

- **Identifiers**

1. CAS No.: 2698-41-1
2. RTECS No.: OO3675000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

o-Chlorobenzylidene malononitrile is a white, crystalline solid with a pepper-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 188.6
2. Boiling point (760 mm Hg): 310° to 315°C (590° to 599°F)
3. Specific gravity (water = 1): Greater than 1 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-chlorobenzylidene malononitrile): 6.5
5. Melting point: 95° to 96°C (203° to 205°F)
6. Vapor pressure at 20°C (68°F): 0.000034 mm Hg
7. Solubility: Insoluble in water; soluble in acetone, benzene, ethyl acetate, dioxane, and methylene chloride.
8. Evaporation rate: Data not available

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Reactivity

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact of o-chlorobenzylidene malononitrile with strong oxidizers causes a violent reaction.

3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine, cyanide, and nitrogen oxides) may be released in a fire involving o-chlorobenzylidene malononitrile.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to o-chlorobenzylidene malononitrile.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: No information is available on the appropriate extinguishant to use for a fire involving o-chlorobenzylidene malononitrile.

Fires involving o-chlorobenzylidene malononitrile should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorobenzylidene malononitrile.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for o-chlorobenzylidene malononitrile is 0.05 ppm parts of air (0.4 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.4 mg/m^3) as a ceiling limit. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned a ceiling limit value of 0.05 ppm (0.39 mg/m^3), which should not be exceeded during any part of the working exposure. The ACGIH has also assigned a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The OSHA, NIOSH, and ACGIH limits are based on the risk of eye and respiratory tract irritation associated with exposure to o-chlorobenzylidene malononitrile [54 Fed. Reg. 2457; NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorobenzylidene malononitrile can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* o-Chlorobenzylidene malononitrile is a severe lacrimator and upper respiratory tract irritant. Human eyes are more sensitive to o-chlorobenzylidene malononitrile-induced irritation than rabbit, rat, or guinea pig eyes; however, even in extreme exposures, eye injuries are superficial and reversible [Grant 1986]. The lowest lethal concentration in rats is 1,806 mg/m^3 for 45 min [NIOSH 1993]. Rats exposed to a 1800-mg/m^3 concentration of this substance for 10 min survived, but a 60-min exposure to 2,700 mg/m^3 killed all of the animals [Hathaway et al. 1991]. The most recent oral LD_{50}s reported for rats are 1,366 mg/kg (male) and 1,284 mg/kg (female) [ACGIH 1991]. Earlier studies in rats reported oral LD_{50}s ranging from 178 to 717 mg/kg [NIOSH 1993]. This substance causes systemic cyanide poisoning when animals are exposed to high doses; the mechanism of action appears to be the release of hydrocyanic acid from one or both nitriles of the malononitrile [Gosselin et al. 1984]. Mice that were injected intraperitoneally or intravenously with o-chlorobenzylidene malononitrile or were exposed

to a concentration of 20,000 mg/m^3/min of the aerosol had cyanide in their blood and urine [ACGIH 1991].

2. *Effects on Humans:* o-Chlorobenzylidene malononitrile (OCBM) is a potent lacrimator and sternutator, and a peripheral sensory irritant in humans. This substance is the active ingredient in tear gas; exposure causes an immediate, disabling irritation of the eyes and respiratory tract in humans, but no OCBM-related deaths have been reported [Grant 1986]. Exposure to an OCBM concentration of 1.5 mg/m^3 for 90 min resulted in headaches in three of four men exposed and caused nose and eye irritation in one man [ACGIH 1991; Hathaway et al. 1991]. Contact of OCBM with the skin resulted in a burning sensation that was greatly aggravated by moisture, erythema, and vesiculation resembling second degree burns were produced [Hathaway et al. 1991]. Workers handling OCBM have developed skin sensitization; the resulting dermatitis involves the arms and neck [ACGIH 1991]. Concentrations of 4.3 to 6.7 mg/m^3 could barely be tolerated when this concentration was reached gradually over a 30-min period; subjects reported conjunctivitis, involuntary closing of the eyes, burning in the throat, cough, and chest constriction [Hathaway et al. 1991]. Concentrations greater than 10 mg/m^3 are extremely irritating and have been found to be intolerable for more than 30 seconds under test conditions; the eye irritation disappeared within an hour after cessation of exposure, and respiratory effects disappeared within a few minutes [Grant 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to o-chlorobenzylidene malononitrile may cause pain and burning of the eyes, excessive tearing, conjunctivitis, involuntary closing of the eyes, excessive salivation, nausea, vomiting, nose and throat irritation, cough, chest constriction, dizziness, headache, and redness and burning of the skin with blister formation.

2. *Chronic exposure:* Chronic exposure to o-chlorobenzylidene malononitrile may cause dermatitis of the face and arms.

- **Emergency procedures:**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water

3. *Inhalation exposure:* Move victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorobenzylidene malononitrile or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do *not* force an unconscious or convulsing person to drink fluid or to vomit

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorobenzyli-

dene malononitrile and may result in worker exposures to this substance:

—Manufacturing and formulation of o-chlorobenzylidene malononitrile for use as a riot control agent

The following methods are effective in controlling worker exposures to o-chlorobenzylidene malononitrile, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to o-chlorobenzylidene malononitrile, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorobenzylidene malononitrile at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorobenzylidene malononitrile exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorobenzylidene malononitrile on the eyes, skin, or respiratory tract. Current health status should be compared with the base-

line health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. o-Chlorobenzylidene malononitrile can be detected in the blood of exposed individuals; however, blood concentrations of this substance do not correlate well with airborne concentrations. Therefore, no biological monitoring test acceptable for routine use has yet been developed for o-chlorobenzylidene malononitrile.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorobenzylidene malononitrile is determined by using a polytetrafluoroethylene (FA) 1-micron filter in series with a Tenax GC tube (70/35-mg sections, 35/60 mesh). Samples are collected at a maximum flow rate of 1.5 liter/min until a maximum air volume of 90 liters is collected. The samples are desorbed with 20% methylene chloride in hexane. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. The limit of detection for this procedure is approximately 0.3 µg/sample. This method is described in NIOSH Method P&CAM 304 of the *NIOSH Manual of Analytical Methods* [NIOSH 1977].

PERSONAL HYGIENE

If o-chlorobenzylidene malononitrile contacts the skin, workers should flush the affected areas immediately with plenty of water, and then wash with soap and water.

Clothing contaminated with o-chlorobenzylidene malononitrile should be removed immediately; provisions should be made for safely removing this chemical from these articles.

A worker who handles o-chlorobenzylidene malononitrile should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where o-chlorobenzylidene malononitrile is handled, processed, or stored.

STORAGE

o-Chlorobenzylidene malononitrile should be stored in a cool, dry, well-ventilated area or in a refrigerator in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorobenzylidene malononitrile should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained o-chlorobenzylidene malononitrile may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorobenzylidene malononitrile, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Ventilate the area of the spill or leak.
4. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.
5. For large spills, build dikes far ahead of the spill to contain the o-chlorobenzylidene malononitrile for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorobenzylidene malononitrile is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of o-chlorobenzylidene malononitrile; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorobenzylidene malononitrile emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorobenzylidene malononitrile is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-chlorobenzylidene malononitrile exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergency situations. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with o-chlorobenzylidene malononitrile. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommenda-

tions, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-chlorobenzylidene malononitrile permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-chlorobenzylidene malononitrile.

If o-chlorobenzylidene malononitrile is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorobenzylidene malononitrile might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorobenzylidene malononitrile. Contact lenses should not be worn if the potential exists for o-chlorobenzylidene malononitrile exposure.

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NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

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Occupational Health Guideline for Chlorobromomethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2BrCl
- Synonyms: Bromochloromethane; methylene chlorobromide; CB; CBM; Halon 1011
- Appearance and odor: Colorless to pale yellow liquid with a characteristic, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorobromomethane is 200 parts of chlorobromomethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1050 milligrams of chlorobromomethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorobromomethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Chlorobromomethane may cause irritation of the eyes and throat. It may also cause mental confusion, dizziness, and unconsciousness.

2. Long-term Exposure: Prolonged or repeated skin exposure may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorobromomethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorobromomethane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from chlorobromomethane exposure.

—Skin disease: Chlorobromomethane can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although chlorobromomethane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although chlorobromomethane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of chlorobromomethane might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Chlorobromomethane vapor is a narcotic and a respiratory irritant. Concentrations near 30,000 ppm were fatal to mice and rats within 15 minutes; this level of exposure produced pulmonary edema and, in delayed deaths, interstitial pneumonitis. The LC50 for mice on 8-hour exposure was 3000 ppm; the predominant observation was narcosis. No toxic effects were observed in several species after repeated inhalation exposures at 1000 ppm for 14 weeks. The substance is a mild skin

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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irritant in animals. A reported exposure of three firefighters to unknown but very high vapor concentrations was characterized by disorientation, headache, nausea, and irritation of the eyes and throat; two of the three became comatose; of these, one had convulsive seizures and the other had respiratory arrest, from which he was resuscitated. Recovery was slow but complete. Some effects may have been due to the inhalation of thermal decomposition products.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 129.4
  2. Boiling point (760 mm Hg): 67.8 C (154 F)
  3. Specific gravity (water = 1): 1.93
  4. Vapor density (air = 1 at boiling point of chlorobromomethane): 4.5
  5. Melting point: −88 C (−126 F)
  6. Vapor pressure at 20 C (68 F): 117 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.9
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Chlorobromomethane reacts with chemically active metals such as calcium, powdered aluminum, zinc, and magnesium.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, carbon monoxide, and hydrogen bromide) may be released when chlorobromomethane decomposes.
  4. Special precautions: Liquid chlorobromomethane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**

Patty states that "chlorobromomethane has a distinctive odor at 400 ppm. It is a good warning at well before acutely hazardous concentration. The odor is distinctive at the acceptable concentration and so gives some warning, but it is not disagreeable enough to drive anyone from the area, and workmen may well tolerate a level well above the acceptable level for chronic exposure."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of chlorobromomethane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chlorobromomethane may be used. An analytical method for chlorobromomethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid chlorobromomethane.
- Non-impervious clothing which becomes wet with liquid chlorobromomethane should be removed promptly and not reworn until the chlorobromomethane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid chlorobromomethane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid chlorobromomethane should be promptly washed or showered with soap or mild detergent and water to remove any chlorobromomethane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorobromomethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a fire extinguishing fluid in vaporizing fire extinguishers; use in manufacture of vaporizing liquid fire extinguishers	Material substitution
Use in mineral and salt separations for flotation	General dilution ventilation; personal protective equipment
Use as a grain fumigant	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If chlorobromomethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If chlorobromomethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlorobromomethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of chlorobromomethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When chlorobromomethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If chlorobromomethane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Chlorobromomethane may be disposed of by absorbing it in vermiculite, dry sand, earth, or a similar material, and disposing in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR CHLOROBROMOMETHANE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLORODIFLUOROMETHANE

INTRODUCTION

This guideline summarizes pertinent information about chlorodifluoromethane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CHClF_2$

- **Synonyms**

  Algeon 22; CFC 22; difluorochloromethane; difluoromonochloromethane; Dymel 22; Fluorocarbon-22; Freon 22; Genetron 22; monochlorodifluoromethane; refrigerant 22; Ucon 22

- **Identifiers**

  1. CAS No.: 75-45-6
  2. RTECS No.: PA6390000
  3. DOT UN: 1018 12
  4. DOT label: Nonflammable gas

- **Appearance and odor**

  Chlorodifluoromethane is a colorless, odorless, nonflammable gas; however, it may be shipped as a liquefied gas under pressure or reduced temperature.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 86.47
  2. Boiling point (760 mm Hg): -40.8°C (-41.4°F)
  3. Specific gravity (water = 1): 1.49 at -69°C (-92.2°F)
  4. Vapor density (air = 1 at boiling point of chlorodifluoromethane): 2.98
  5. Melting point: -146°C (-230.8°F)
  6. Vapor pressure at 21°C (70°F): 7,121.2 mm Hg
  7. Solubility: Very soluble in water; soluble in ether, acetone, and chloroform
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: Contact of chlorodifluoromethane at high temperatures with alkalies or alkaline earth

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metals such as aluminum, sodium, potassium, or zinc causes thermal decomposition.

3. Hazardous decomposition products: Toxic gases (such as fluorine, chlorine, phosgene, and carbonyl halides) may be released in a fire involving chlorodifluoromethane.

4. Special precautions: Corrosion can occur when magnesium alloys or aluminum containing more than 2% magnesium is used with fluorocarbon systems in which water may be present.

Flammability

The National Fire Protection Association has not assigned a flammability rating to chlorodifluoromethane; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving chlorodifluoromethane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chlorodifluoromethane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorodifluoromethane. Structural firefighters' protective clothing may provide limited protection against fires involving chlorodifluoromethane.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chlorodifluoromethane [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1,000 ppm (3,500 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 1,250 ppm (4,375 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure limit that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorodifluoromethane a threshold limit value (TLV) of 1,000 ppm (3,540 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of cardiac sensitization, asphyxiation, and central nervous system effects associated with exposure to chlorodifluoromethane.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorodifluoromethane can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chlorodifluoromethane causes depression of the central nervous system, cardiac arrhythmias, and asphyxiation. The LC_{50} in the rat is 35 parts per hundred (pph) (350,000 ppm) for a 15-min exposure; acutely poisoned animals exhibited altered sleep times, stumbling, and respiratory depression before death [NIOSH 1989]. Mice exposed for 2-hr periods showed a maximum tolerated concentration of 320,000 ppm, and a minimum fatal level of 370,000 ppm [ACGIH 1991]. Rats and guinea pigs exposed by inhalation to airborne concentrations of 75,000 to 100,000 ppm chlorodifluoromethane for 2-hr showed excitation and/or changes in equilibrium; narcosis occurred at 200,000 ppm and death occurred at 300,000 and

400,000 ppm [ACGIH 1991]. Dogs exposed to a 50,000-ppm concentration of chlorodifluoromethane developed cardiac sensitization; exposure to 25,000 ppm did not cause this effect [ACGIH 1991]. The minimum concentration capable of altering the reflex response in rabbits varied between 11,000 and 20,000 ppm [ACGIH 1991]. In 2-hr exposures to guinea pigs, the highest concentration tested (200,000 ppm) did not cause death, while 50,000 ppm produced mild clinical changes, and minimal effects were noted at 25,000 ppm [ACGIH 1991]. In a 4-week study in which rats, guinea pigs, dogs, and cats were exposed to a 50,000-ppm concentration of chlorodifluoromethane for twenty 3.5-hr episodes, no clinical, biochemical, or pathological effects were observed [ACGIH 1991]. Rats, mice, and rabbits were exposed for 6 hr/day, 6 days/week for 10 months to 14,000 ppm chlorodifluoromethane. In another experiment, rats and mice were exposed to 2,000 ppm of this substance for the same period. No effects were noted in animals exposed at the lower concentration, but at 14,000 ppm, alterations occurred in body weight, physiological endurance, and hematological characteristics; pathological changes were noted in the lungs, central nervous system, heart, liver, kidneys, and spleen [ACGIH 1991]. In one inhalation bioassay in rats, males exposed to the highest concentration administered showed only a marginal increase in the incidence of subcutaneous fibrosarcomas and Zymbal-gland tumors, and negative results were obtained for females [IARC 1987]. Based on this study, the International Agency for Research on Cancer (IARC) has concluded that the evidence for chlorodifluoromethane's carcinogenicity in animals is limited [IARC 1987].

2. *Effects on Humans:* In humans, chlorodifluoromethane can affect the heart; at very high concentrations, it is an asphyxiant. A study of hospital personnel exposed to 300 ppm chlorodifluoromethane during tissue freezing procedures revealed a 3.5-fold increase in the incidence of palpitations in exposed individuals over the incidence in nonexposed hospital personnel [Clayton and Clayton 1981; Hathaway et al. 1991]. An epidemiologic study involving workers exposed to chlorofluorocarbons, including chlorodifluoromethane, showed no increased mortality due to heart, circulatory, or malignant disorders [Hathaway et al. 1991]. A small study of 539 refrigeration workers exposed to a mixture of chlorofluorocarbons, including chlorodifluoromethane, for at least 6 months and followed for up to 30 years was inconclusive, leading IARC to conclude that the evidence for the carcinogenicity of this substance in humans is inadequate [IARC 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Chlorodifluoromethane may cause dizziness, disorientation, incoordination, narcosis, nausea, vomiting, heart palpitations (irregular heart beat), tightness in the chest, and difficult breathing. Direct tissue contact with liquid chlorodifluoromethane may cause frostbite.

2. *Chronic exposure:* Continued low-level exposure to chlorodifluoromethane may cause an irregular heartbeat.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of frostbite, toxicity, or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* If tissue is frozen, seek medical attention ***immediately***; do not rub the affected areas or flush them with water. If tissue is not frozen, immediately and thoroughly wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from fur-

ther exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorodifluoromethane and may result in worker exposures to this substance:

—Formulation of aerosol propellants (former use)

—Use as a component of fluorocarbon resins (such as tetrafluoroethylene polymers) and as a low-temperature solvent

—Use in central air conditioning systems and heat pumps

—Use in cylinder packing and shipping and tank car filling

The following methods are effective in controlling worker exposures to chlorodifluoromethane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chlorodifluoromethane, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the cardiovascular system.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chlorodifluoromethane at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and

other findings consistent with diseases of the cardiovascular system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorodifluoromethane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorodifluoromethane on the cardiovascular system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chlorodifluoromethane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorodifluoromethane is determined by using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.05 liter/min or less until a maximum air volume of 1 liter is collected. The sample is then treated with carbon disulfide to extract the chlorodifluoromethane. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1989] and in the *OSHA Chemical Information Manual* [OSHA 1991].

PERSONAL HYGIENE

If liquid chlorodifluoromethane contacts the skin, workers should flush the affected areas immediately with plenty of tepid water for 15 min, and then wash with soap and water.

Clothing contaminated with liquid chlorodifluoromethane should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles cylinders of liquid chlorodifluoromethane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorodifluoromethane is handled, processed, or stored.

STORAGE

Chlorodifluoromethane should be stored in a cool, dry, well-ventilated area in closed, pressurized, steel containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chlorodifluoromethane should be protected from physical damage and should be stored separately from alkaline earth metals (such as sodium, aluminum, or potassium), heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorodifluoromethane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chlorodifluoromethane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chlorodifluoromethane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorodifluoromethane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chlorodifluoromethane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorodifluoromethane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with liquid chlorodifluoromethane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against chlorodifluoromethane and have demonstrated resistance: Natural rubber and neoprene. Nitrile, polyvinylchloride, and styrene-butadiene rubber have demonstrated poor resistance to permeation by chlorodifluoromethane.

If liquid chlorodifluoromethane is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which liquid chlorodifluoromethane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with liquid chlorodifluoromethane. Contact lenses should not be worn if the potential exists for chlorodifluoromethane exposure.

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Occupational Health Guideline for Chlorodiphenyl (42% Chlorine)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{12}H_7Cl_5$ (approximately)
- Synonyms: Polychlorinated biphenyl; PCB
- Appearance and odor: Colorless to dark liquid with a mild hydrocarbon odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorodiphenyl (42% chlorine) is 1 milligram of chlorodiphenyl (42% chlorine) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for polychlorinated biphenyls be reduced to 1.0 microgram per cubic meter of air averaged over a work shift of up to 10 hours per day, 40 hours per week, and that chlorodiphenyl (42% chlorine) be regulated as an occupational carcinogen. The NIOSH Criteria Document for Polychlorinated Biphenyls should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorodiphenyl (42% chlorine) can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Chlorodiphenyl (42% chlorine) may cause irritation of the eyes, nose, and throat, and an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, and yellow jaundice. Repeated skin contact with the liquid may cause skin irritation. The production of liver tumors and adverse reproductive effects has been demonstrated in experimental animals following ingestion of polychlorinated biphenyls. The relevance to humans of some of these studies has not yet been established.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorodiphenyl (42% chlorine).

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorodiphenyl (42% chlorine) at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and skin should be stressed. The skin should be examined for evidence of chronic disorders. Women in the work force should be advised of the potential adverse effects of chlorodiphenyl (42% chlorine) on the unborn child. Those who have borne children and work with chlorodiphenyl (42% chlorine) should be counseled concerning the advisability of nursing their offspring.

—Liver function tests: Chlorodiphenyl (42% chlorine) may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Chlorodiphenyl (42% chlorine) is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

• **Summary of toxicology**

Chlorodiphenyl (42% chlorine) vapor is toxic to the liver and causes an acne-form dermatitis (chloracne). Guinea pigs died at intervals up to 21 days after the first of 11 daily applications of 34.5 mg to the skin and, at necropsy, the liver showed fatty degeneration and central atrophy; rats, however, survived 25 daily applications, and only slight changes in the liver were observed. The vapor and liquid are moderately irritating to eye tissues. Cases of mild to moderate skin irritation with an acne-form eruption have been reported in workers exposed to 0.1 mg/m^3; levels of 10 mg/m^3 were unbearably irritating. Several deaths due to atrophy of the liver have occurred among workers exposed to the fumes of chlorodiphenyls and chloronaphthalenes. The production of liver tumors and adverse reproductive effects has been demonstrated in experimental animals following ingestion of polychlorinated biphenyls. The relevance to humans of some of these studies has not yet been established.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 257.5 (approximately)
2. Boiling point (760 mm Hg): 325– 366 C (617–691 F)
3. Specific gravity (water = 1): 1.38
4. Vapor density (air = 1 at boiling point of chlorodiphenyl (42% chlorine)): 8.9
5. Melting point: –19 C (-2 F) (pour point)
6. Vapor pressure at 20 C (68 F): 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much less than 1

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving chlorodiphenyl (42% chlorine).
4. Special precautions: Chlorodiphenyl (42% chlorine) will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 176 C (349 F)
2. Autoignition temperature: None to boiling point
3. Flammable limits in air, % by volume: Not available
4. Extinguishant: Foam, dry chemical, carbon dioxide

• **Warning properties**

According to the AIHA *Hygienic Guide*, chlorodiphenyl (42% chlorine) has a typical aromatic odor and causes eye irritation. For the purposes of this guideline, however, it is treated as a material with poor warning properties, as no quantitative data are available concerning its odor and irritation thresholds. As stated in the AIHA *Hygienic Guide*, the vapors of the chlorodiphenyls are "moderately irritating to eye tissues." The concentrations causing eye irritation are not mentioned.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of chlorodiphenyl (42% chlorine) on a glass fiber filter connected in a series with a midget bubbler containing iso-octane, followed by gas chromatographic analysis. A detailed analytical method for chlorodiphenyl (42% chlorine) may be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, under the title "NIOSH Analytical Methods for Set 2" (order number PB 271

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorodiphenyl (42% chlorine).

• Clothing contaminated with liquid chlorodiphenyl (42% chlorine) should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlorodiphenyl (42% chlorine) from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorodiphenyl (42% chlorine), the person performing the operation should be informed of chlorodiphenyl's (42% chlorine) hazardous properties.

• Non-impervious clothing which becomes contaminated with liquid chlorodiphenyl (42% chlorine) should be removed promptly and not reworn until the chlorodiphenyl (42% chlorine) is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid chlorodiphenyl (42% chlorine) may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid chlorodiphenyl (42% chlorine) should be promptly washed or showered with soap or mild detergent and water to remove any chlorodiphenyl (42% chlorine).

• Eating and smoking should not be permitted in areas where liquid chlorodiphenyl (42% chlorine) is handled, processed, or stored.

• Employees who handle liquid chlorodiphenyl (42% chlorine) should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

• Areas in which exposure to chlorodiphenyl (42% chlorine) may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorodiphenyl (42% chlorine) may occur and control methods which may be effective in each case:

Operation	Controls
Use as high-temperature transfer medium in chemical/food processing vessels and drying ovens	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a dielectric in manufacture of transformers, capacitors, resistors, and other electrical apparatus	General dilution ventilation; local exhaust ventilation; personal protective equipment
Application and formulation as plasticizer, flame-retardant, and adhesive and weatherizer in spray surface coatings; manufacture and application of impregnants for cloth, paper, fiberboard, wood, and asbestos; manufacture and application of natural and synthetic waxes and polishes; manufacture and application of hot-melt and other adhesives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as non-flammable working fluid in vacuum pumps, hydraulic systems, and expansion systems	General dilution ventilation; local exhaust ventilation
Use during application of high-pressure, temperature, and moisture lubricants	Personal protective equipment
Use in compounding and processing of plastics for flame retardancy	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture and application for use as pesticides and fungicides	Personal protective equipment
Use as an intermediate or raw material in further organic synthesis	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as sealer for gaskets of natural rubber and synthetics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as adhesive release on tapes and ink release on carbonless duplicating paper; as a pigment carrier in dyeing polyesters and paper	Personal protective equipment

Use as a pressure adhesive for sign backings, insect traps, and tapes	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in compounding mastics, and sealing and caulking materials; use in compounding of printing inks	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If chlorodiphenyl (42% chlorine) gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If chlorodiphenyl (42% chlorine) gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlorodiphenyl (42% chlorine) soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of chlorodiphenyl (42% chlorine), move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When chlorodiphenyl (42% chlorine) has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If chlorodiphenyl (42% chlorine) is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Chlorodiphenyl (42% chlorine) may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

REFERENCES

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 7, 1974, and Volume 18, 1978.

RESPIRATORY PROTECTION FOR CHLORODIPHENYL (42% CHLORINE)

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Vapor Concentration	
10 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against pesticides. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorodiphenyl (42% chlorine); however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 10 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chlorodiphenyl (54% Chlorine)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{12}H_5Cl_5$ (approximately)
- Synonyms: Polychlorinated biphenyl; PCB
- Appearance and odor: Pale yellow viscous liquid with a mild hydrocarbon odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorodiphenyl (54% chlorine) is 0.5 milligram of chlorodiphenyl (54% chlorine) per cubic meter of air (mg/m³) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for polychlorinated biphenyls be reduced to 1.0 microgram per cubic meter of air averaged over a work shift of up to 10 hours per day, 40 hours per week, and that chlorodiphenyl (54% chlorine) be regulated as an occupational carcinogen. The NIOSH Criteria Document for Polychlorinated Biphenyls should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorodiphenyl (54% chlorine) can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Chlorodiphenyl (54% chlorine) may cause irritation of the eyes, nose, and throat, and an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, and yellow jaundice. Repeated skin contact with the liquid may cause skin irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorodiphenyl (54% chlorine). The production of liver tumors and adverse reproductive effects have been demonstrated in experimental animals following ingestion of polychlorinated biphenyls. The relevance to humans of some of these studies has not yet been established.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorodiphenyl (54% chlorine) at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and skin should be stressed. Women in the work force should be advised of the potential adverse effects of chlorodiphenyl (54% chlorine) on the unborn child. Those who have borne children and work with chlorodiphenyl (54% chlorine) should be counseled concerning the advisability of nursing their offspring.

—Liver function tests: Chlorodiphenyl (54% chlorine) may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Chlorodiphenyl (54% chlorine) is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

• **Summary of toxicology**

Chlorodiphenyl (54% chlorine) vapor is toxic to the liver. Rats exposed to 5.4 mg/m³ for 7 hours daily for 4 months showed increased liver weight and injury to the liver cells; 1.5 mg/m³ for 7 months also produced histopathologic evidence of liver damage, which was considered to be of a reversible character. The vapor and the liquid are moderately irritating to the eye; contact with skin leads to removal of natural fats and oils with subsequent drying and cracking of the skin. Acne-form dermatitis (chloracne) due to exposure to chlorodiphenyl of 54% chlorine content has been reported but the period of exposure was not indicated. The production of liver tumors and adverse reproductive effects has been demonstrated in experimental animals following ingestion of polychlorinated biphenyls. The relevance to humans of some of these studies has not yet been established.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 326 (approximately)
2. Boiling point (760 mm Hg): 365– 390 C (689–734 F)
3. Specific gravity (water = 1): 1.5
4. Vapor density (air = 1 at boiling point of chlorodiphenyl (54% chlorine)): 11.2
5. Melting point: 10 C (50 F) (pour point)
6. Vapor pressure at 20 C (68 F): 0.00006 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much less than 1

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving chlorodiphenyl (54% chlorine).
4. Special precautions: Chlorodiphenyl (54% chlorine) will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 222 C (432 F)
2. Autoignition temperature: None to boiling point
3. Flammable limits in air, % by volume: Not available
4. Extinguishant: Foam, dry chemical, carbon dioxide

• **Warning properties**

Although chlorodiphenyl (54% chlorine) has a typical aromatic odor and causes eye irritation, this substance is treated as a material with poor warning properties, as no quantitative information is available concerning its odor and irritation thresholds. The AIHA *Hygienic Guide* states that the vapors of the chlorodiphenyls are "moderately irritating to eye tissues," but the concentrations which cause irritation are not stated.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of chlorodiphenyl on a filter with subsequent extraction with petroleum ether and gas chromatographic analysis. An analytical method for chlorodiphenyl (54% chlorine) is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid chlorodiphenyl (54% chlorine).

• Clothing contaminated with liquid chlorodiphenyl (54% chlorine) should be placed in closed containers for storage until it can be discarded or until provision is

made for the removal of chlorodiphenyl (54% chlorine) from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorodiphenyl (54% chlorine), the person performing the operation should be informed of chlorodiphenyl's (54% chlorine) hazardous properties.

- Non-impervious clothing which becomes contaminated with liquid chlorodiphenyl (54% chlorine) should be removed promptly and not reworn until the chlorodiphenyl (54% chlorine) is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid chlorodiphenyl (54% chlorine) may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid chlorodiphenyl (54% chlorine) should be promptly washed or showered with soap or mild detergent and water to remove any chlorodiphenyl (54% chlorine).
- Eating and smoking should not be permitted in areas where liquid chlorodiphenyl (54% chlorine) is handled, processed, or stored.
- Employees who handle liquid chlorodiphenyl (54% chlorine) should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Areas in which exposure to chlorodiphenyl (54% chlorine) may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorodiphenyl (54% chlorine) may occur and control methods which may be effective in each case:

Operation	Controls
Use as high-temperature transfer medium in chemical/food processing vessels and drying ovens	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a dielectric in manufacture of transformers, capacitors, resistors, and other electrical apparatus	General dilution ventilation; local exhaust ventilation; personal protective equipment
Application and formulation as plasticizer, flame-retardant, and adhesive and weatherizer in spray surface coatings; manufacture and application of impregnants for cloth, paper, fiberboard, wood, and asbestos; manufacture and application of natural and synthetic waxes and polishes; manufacture and application of hot-melt and other adhesives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as non-flammable working fluid in vacuum pumps, hydraulic systems, and expansion systems	General dilution ventilation; local exhaust ventilation
Use during application of high-pressure, temperature, and moisture lubricants	Personal protective equipment
Use in compounding and processing of plastics for flame retardancy	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture and application for use as pesticides and fungicides	Personal protective equipment
Use as an intermediate or raw material in further organic synthesis	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as sealer for gaskets of natural rubber and synthetics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as adhesive release on tapes and ink release on carbonless duplicating paper; as a pigment carrier in dyeing polyesters and paper	Personal protective equipment

Use as a pressure adhesive for sign backings, insect traps, and tapes	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in compounding mastics, and sealing and caulking materials; use in compounding of printing inks	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If chlorodiphenyl (54% chlorine) gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If chlorodiphenyl (54% chlorine) gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If chlorodiphenyl (54% chlorine) soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of chlorodiphenyl (54% chlorine), move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When chlorodiphenyl (54% chlorine) has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If chlorodiphenyl (54% chlorine) is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Chlorodiphenyl (54% chlorine) may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on chlorodiphenyl (54% chlorine), look up chlorodiphenyl (54% chlorine) in the following documents:

• Medical Surveillance from the SCP
• Respiratory Protection from the SCP
• Personal Protection and Sanitation from the SCP
• NIOSH Criteria Document for Polychlorinated Biphenyls (September 1977)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 7, 1974, and Volume 18, 1978.

RESPIRATORY PROTECTION FOR CHLORODIPHENYL (54% CHLORINE)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Vapor Concentration	
5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against pesticides. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorodiphenyl (54% chlorine); however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 5 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Chloroform*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CHCl_3$
- Synonyms: Trichloromethane
- Appearance and odor: Colorless liquid with a pleasant, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chloroform is a ceiling level of 50 parts of chloroform per million parts of air (ppm). This may also be expressed as 240 milligrams of chloroform per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 2 ppm averaged over a one-hour period, and that chloroform be regulated as an occupational carcinogen. The NIOSH Criteria Document for Chloroform should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chloroform can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Chloroform vapor may cause headache, drowsiness, vomiting, dizziness, unconsciousness, irregular heart beat, and death. Liver and kidney damage may also result from exposure to chloroform vapor. When splashed in the eye, chloroform causes pain and irritation. Swallowing chloroform is followed immediately by severe burning of the mouth and throat, pain in the chest and abdomen, and vomiting. Depending on the amount swallowed, loss of consciousness and liver damage may follow.

2. Long-term Exposure: Prolonged exposure to chloroform may cause liver and kidney damage. Prolonged or repeated skin contact with the liquid may produce skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chloroform.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chloroform at potentially hazardous levels:

1. Initial Medical Examination:

— A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. A history of, or physical signs consistent with, chronic alcoholism probably constitutes such an increased risk. Examination of liver, kidneys, and heart should be stressed. The skin should be examined for evidence of chronic disorders.

— Liver function tests: A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

— Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Chloroform vapor is a central nervous system depressant and is toxic to the liver and kidneys. It has been largely abandoned as an anesthetic agent because of the frequency of cardiac arrest during surgery and of

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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delayed death due to hepatic injury. An increased incidence of cardiac arrhythmias has been demonstrated during surgery in patients anesthetized with chloroform, as compared with other anesthetic agents; vapor concentrations were of the order of 22,500 ppm. Animals showed minor and reversible injury of liver and kidneys after repeated 7-hour exposures to concentrations of chloroform as low as 25 ppm, while 50 to 85 ppm produced more severe injury. Experimental human exposures showed that 14,000 to 16,000 ppm caused rapid loss of consciousness in man; 4100 ppm or less caused serious disorientation, while single exposures of 1000 ppm caused dizziness, nausea, and aftereffects of fatigue and headache. Prolonged exposure to 80 to 240 ppm caused lassitude, digestive disturbances, and mental dullness, while 20 to 70 ppm produced milder symptoms. Of 68 chemical workers exposed regularly to concentrations of 2 to 205 ppm for 1 to 4 years, some 25% had hepatomegaly. This group of 68 exposed workers were found to be more susceptible to viral hepatitis than the general population. The hepatotoxicity of several chlorinated hydrocarbons has been shown to be potentiated by prior exposure to some aliphatic alcohols. This phenomenon has been demonstrated in mice exposed first to isopropyl alcohol by gavage and then to chloroform by intraperitoneal injection. A potentiating effect of ethyl alcohol ingestion on the toxicity of chloroform vapor in the occupational setting is suspected, but has not been proven in industrial practice. High concentrations of vapor cause conjunctival irritation and blepharospasm. Liquid chloroform splashed in the eye causes immediate burning pain and conjunctival irritation; the corneal epithelium may be injured, but regeneration is prompt, and the eye returns to normal in 1 to 3 days. The liquid has a defatting effect on the skin and may produce chronic irritation with drying and cracking. Liver tumors have been reported in animals.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 119.4
2. Boiling point (760 mm Hg): 61 C (142 F)
3. Specific gravity (water = 1): 1.49
4. Vapor density (air = 1 at boiling point of chloroform): 4.1
5. Melting point: −63.5 C (−82 F)
6. Vapor pressure at 20 C (68 F): 160 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.8
8. Evaporation rate (butyl acetate = 1): 11.6

- **Reactivity**

1. Conditions contributing to instability: In the presence of air and light, chloroform slowly reacts to form toxic phosgene and hydrogen chloride gases.
2. Incompatibilities: Chloroform reacts with strong caustics and chemically active metals such as aluminum, magnesium powder, sodium, or potassium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, phosgene, and carbon monoxide) may be released when chloroform decomposes.
4. Special precautions: Liquid chloroform will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Patty reports that the odor threshold of chloroform is approximately 200 to 300 ppm, and May reports an odor threshold of 200 ppm. The *Hygienic Guide*, however, gives an odor threshold of 50 ppm and states that "olfactory fatigue" occurs upon exposure.
2. Eye Irritation Level: Grant states that "in conscious individuals high concentrations of vapors of chloroform cause moderate sensation of stinging and irritation of the eyes, automatically inducing protective closure of the lids." The concentrations causing eye irritation are not mentioned. However, Patty does not give any indication that eye irritation occurs at concentrations even as high as 4096 ppm.
3. Evaluation of Warning Properties: Since there are no quantitative data relating the irritant effects of chloroform to air concentrations, and since olfactory fatigue occurs during exposure to chloroform, this material is treated as a substance with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **One-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average one-hour exposure is based on a single one-hour sample. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chloroform. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chloroform may be used. An

analytical method for chloroform is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid chloroform, where skin contact may occur.
- Clothing wet with liquid chloroform should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chloroform from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chloroform, the person performing the operation should be informed of chloroform's hazardous properties.
- Non-impervious clothing which becomes wet with liquid chloroform should be removed promptly and not reworn until the chloroform is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid chloroform may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to chloroform, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid chloroform should be promptly washed or showered with soap or mild detergent and water to remove any chloroform.
- Eating and smoking should not be permitted in areas where liquid chloroform is handled, processed, or stored.
- Employees who handle liquid chloroform should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.
- Areas in which exposure to chloroform may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chloroform may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of fluorocarbons for refrigerant propellants; manufacture of fluorocarbon resins	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as an extractant solvent in manufacure of pharmaceuticals, rubber, essential oils and flavors, sterols and alkaloids, and in the recovery of fat from waste products	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in chemical analysis and assays; veterinary uses, and in standard solutions as preservative and bactericide	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a general solvent in plastics, dyes, oils, waxes, rubber, cleaning and dry cleaning industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in dye, drug, and pesticide industries	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chloroform gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If burning is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If chloroform gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chloroform soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of chloroform, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When chloroform has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If chloroform is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

ADDITIONAL INFORMATION

To find additional information on chloroform, look up chloroform in the following documents:

• Medical Surveillance for Chemical Hazards

• Respiratory Protection for Chemical Hazards

• Personal Protection and Sanitation for Chemical Hazards

• NIOSH Criteria Document for Chloroform (Revised June 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Chloroform," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 1, 1972.

RESPIRATORY PROTECTION FOR CHLOROFORM

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR bis-CHLOROMETHYL ETHER POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about bis-chloromethyl ether for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_2H_4Cl_2O$
- **Structure:** $ClCH_2OCH_2Cl$
- **Synonyms:** bis(Chloromethyl) ether; bis-CME; chloro-(chloromethoxy) methane; chloromethyl ether; sym-dichloro-dimethyl ether; sym-dichloromethyl ether; dimethyl-1'-dichloroether; oxybis(chloromethane)
- **Identifiers:** CAS 542-88-1; RTECS KN1575000; DOT 2249, label required: "Poison, Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a suffocating odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.96
2. Boiling point (at 760 mmHg): 106°C (223°F)
3. Specific gravity (water = 1): 1.315
4. Vapor density (air = 1 at boiling point of bis-chloromethyl ether): 3.97
5. Melting point: -41.5°C (-42.7°F)

- **Reactivity**

1. Incompatibilities: bis-Chloromethyl ether is very volatile and may cause fire if exposed to excessive heat; bis-chloromethyl ether hydrolyzes in water to form hydrogen chloride and formaldehyde.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide, hydrogen chloride, and formaldehyde) may be released in a fire involving bis-chloromethyl ether.
3. Caution: Hydrogen chloride and formaldehyde react to form bis-chloromethyl ether under certain conditions of temperature and humidity. Any reaction in which these two compounds are present should be investigated for bis-chloromethyl ether formation.

- **Flammability**

Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for bis-chloromethyl ether; however, the OSHA standard requires implementation of stringent controls wherever bis-chloromethyl ether or solid or liquid mixtures containing at least 0.1% by weight or volume of bis-chloromethyl ether are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations 29 CFR 1910.1008, bis-Chloromethyl Ether. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated bis-chloromethyl ether as an A-1 substance (confirmed human carcinogen) having a TLV of 0.001 parts of bis-chloromethyl ether per million parts of air (ppm) [0.005 milligram per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek.

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HEALTH HAZARD INFORMATION

• Routes of exposure
bis-Chloromethyl ether may cause adverse health effects following exposure via inhalation, or dermal or eye contact.

• Summary of toxicology
1. *Effects on animals:* Acute inhalation of bis-chloromethyl ether vapor by rats or hamsters caused pulmonary congestion, edema, and hemorrhage. Chronic inhalation of bis-chloromethyl ether by rats or mice produced cancers of the lungs, nasal cavity, or skin.
2. *Effects on humans:* Chronic inhalation of bis-chloromethyl ether has produced lung cancer and a reduction in pulmonary function.

• Signs and symptoms of exposure
1. *Short-term (acute):* bis-Chloromethyl ether vapor is highly irritating to the skin and eyes and to the mucous membranes of the respiratory tract. Liquid bis-chloromethyl ether can cause burns and tissue destruction (necrosis).
2. *Long-term (chronic):* Inhalation of bis-chloromethyl ether can cause breathing difficulty (dyspnea), wheezing, pulmonary hemorrhage, and increased bronchial secretions.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation
Prior to placing a worker in a job with a potential for exposure to bis-chloromethyl ether, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to bis-chloromethyl ether. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and lung dysfunction.

• Periodic medical screening and/or biologic monitoring
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to bis-chloromethyl ether. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function. Because bis-chloromethyl ether is highly irritating to the skin and mucous membranes, the examining physician should be cognizant of any changes in the condition of the skin or signs of contact and/or allergic dermatitis.

• Medical practices recommended at the time of job transfer or termination
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to bis-chloromethyl ether may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events
1. Acute SHE's include: Contact and/or allergic dermatitis
2. Delayed-onset SHE's include: Cancer of the trachea, bronchi, and lungs

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting bis-chloromethyl ether vapors with Chromosorb 101 in short tubes followed by desorption with helium through a gas chromatographic column and analysis by mass spectroscopy. Direct-reading devices calibrated to measure bis-chloromethyl ether may also be used if available. Detailed sampling and analytical methods for bis-chloromethyl ether may be found in the *NIOSH Manual of Analytical Methods* (method numbers 213, 220).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory type hoods" or in locations where bis-chloromethyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where bis-chloromethyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with bis-chloromethyl ether should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of bis-chloromethyl ether from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of bis-chloromethyl ether's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove bis-chloromethyl ether from materials and equipment. Contaminated materials should be removed from regulated areas without further contamination of the facility.

OSHA requires that workers wash their faces, necks, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

In regulated areas, OSHA prohibits the storage or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage of use of products for chewing.

OSHA prohibits the location of drinking fountains in regulated areas.

GENERAL CONTROL PROCEDURES

The following control procedures are derived from OSHA requirements as stated in 29 CFR 1910.1008:

Areas where bis-chloromethyl ether is manufactured, processed, used, repackaged, released, handled, or stored shall be designated as regulated areas, and entry into and exit from these areas shall be restricted and controlled. Only authorized workers shall be permitted access to regulated areas.

Workers authorized to enter regulated areas shall receive a training and indoctrination program including but not limited to the nature of the carcinogenic hazards of bis-chloromethyl ether, including local and systemic toxicity, the specific nature of the operation which could result in exposure, and the purpose for and the significance of decontamination and emergency practices and procedures.

Entrances to regulated areas shall be posted with signs indicating that a cancer-suspect agent is present and that only authorized workers wearing appropriate protective clothing and equipment shall be admitted.

Appropriate signs and instructions shall be posted at the entrance to and exit from regulated areas to inform workers of the procedures that must be followed when entering or leaving a regulated area.

Open vessel system operations involving bis-chloromethyl ether which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of bis-chloromethyl ether into regulated areas, non-regulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where bis-chloromethyl ether is contained in an other-

wise "closed system" but is transferred, charged, or discharged into other normally closed containers, each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas, or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

Containers of bis-chloromethyl ether shall be identified as to contents and shall contain a hazard warning.

Regulated areas (with the exception of outdoor operations) shall be operated under negative pressure with respect to nonregulated areas. Local exhaust ventilation may be used to satisfy this requirement. Clean makeup air in equal volume shall replace air that is removed.

The introduction or removal of any equipment, materials, or other items to or from a regulated area shall be done in a manner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove bis-chloromethyl ether from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to bis-chloromethyl ether may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for bis-chloromethyl ether

Operations	Controls
During use in the manufacture of ion-exchange resins and polymers; during use as a solvent for polymerization reactions and as a chloromethylation agent in chemical synthesis; during use in the treatment of textiles	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substances

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures. If a worker has contact with bis-chloromethyl ether, OSHA requires that the worker shower as soon as possible, unless contraindicated by physical injuries.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to bis-chloromethyl ether, an eye-wash fountain should be provided within the immediate work area for emergency use.

If bis-chloromethyl ether gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to bis-chloromethyl ether, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If bis-chloromethyl ether gets on the skin, wash it immediately with soap and water. If bis-chloromethyl ether penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

OSHA requires that affected areas of spills or leaks be evacuated as soon as an emergency has been determined.

OSHA requires that only authorized workers provided with and wearing clean, impervious garments (including gloves, boots, and continuous air-supplied hoods) enter areas of spills or leaks.

OSHA requires that workers authorized to enter areas of spills or leaks be decontaminated before removing the protective garments and hoods and before showering.

If bis-chloromethyl ether is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing bis-chloromethyl ether, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing bis-chloromethyl ether may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing bis-chloromethyl ether may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for bis-chloromethyl ether

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROMETHYL METHYL ETHER POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about chloromethyl methyl ether for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_2H_5ClO
- **Structure:** $ClCH_2OCH_3$
- **Synonyms:** Methyl chloromethyl ether, CMME, dimethylchloroether
- **Identifiers:** CAS 107-30-2; RTECS KN6650000; DOT 1239, label required: "Flammable Liquid"
- **Appearance:** Clear, colorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 80.52
2. Boiling point (at 760 mm Hg): 59.1°C (138.6°F)
3. Specific gravity (water = 1): 1.0625
4. Vapor density (air = 1 at boiling point of chloromethyl methyl ether): 2.77
5. Melting point: -103.5°C (-154.3°F)

- **Reactivity**

1. Incompatibilities: Cloromethyl methyl ether will react with surface moisture to evolve hydrogen chloride which is corrosive to metal.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving chloromethyl methyl ether.
3. Caution: Technical grade chloromethyl methyl ether may contain 1-8% bis-chloromethyl ether, a potential human carcinogen. Chloromethyl methyl ether decomposes to hydrogen chloride and formaldehyde which can, under proper temperature and humidified conditions, form bis-chloromethyl ether.

- **Flammability**

1. Flash point: -17.8°C (0°F) (open cup)
2. Extinguishant: Dry chemical, foam, or carbon dioxide
3. Class IB Flammable Liquid (29 CFR 1910.106)

- **Warning properties**

1. Eye irritation levels: Chloromethyl methyl ether is severely irritating to the eyes and skin at 100 ppm.
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) does not have a specific permissible exposure limit (PEL) for chloromethyl methyl ether; however, the OSHA standard requires implementation of stringent controls wherever chloromethyl methyl ether or solid or liquid mixtures containing at least 0.1% by weight or volume of chloromethyl methyl ether are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1006, Methyl Chloromethyl Ether. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated chloromethyl methyl ether as an A2 substance (suspected human carcinogen) without having sufficient evidence to assign a threshold limit value (TLV®).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chloromethyl methyl ether may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* Chronic subcutaneous injection of mice with chloromethyl methyl ether containing bis-chloromethyl ether produced skin cancer; chronic inhalation produced lung cancer.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

2. *Effects on humans:* Acute exposure to chloromethyl methyl ether vapor has caused corneal damage, pulmonary edema, pulmonary congestion, and pneumonia. Dermal exposure to liquid chloromethyl methyl ether has caused burns and tissue destruction (necrosis). Exposure to technical grade chloromethyl methyl ether, which is commonly contaminated with bis-chloromethyl ether (1-8%), has been associated with an increased incidence of lung cancer.

• Signs and symptoms of exposure

1. *Short-term (acute):* Inhalation exposure to chloromethyl methyl ether can cause severe respiratory impairment, sore throat, fever, and chills. Chloromethyl methyl ether is also highly irritating to the mucous membranes, eyes, and skin.
2. *Long-term (chronic):* Inhalation of chloromethyl methyl ether can cause coughing, wheezing, blood-stained sputum, breathing difficulty (dyspnea), and weight loss.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to chloromethyl methyl ether, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to chloromethyl methyl ether at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to chloromethyl methyl ether. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin and respiratory system as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to chloromethyl methyl ether may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Cancer of the respiratory tract (trachea, bronchi, and lungs).

MONITORING AND MEASUREMENT PROCEDURES

• Method

Sampling and analysis may be performed by collecting chloromethyl methyl ether vapors with glass impingers followed by extraction with hexane and analysis by electron-capture gas chromatography. Direct-reading devices calibrated to measure chloromethyl methyl ether may also be used if applicable. A detailed sampling and analytical method for chloromethyl methyl ether may be found in the *NIOSH Manual of Analytical Methods* (method number 220).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the

manufacturer, and then evaluating the clothing under actual use conditions.

In operations involving "laboratory-type hoods" or in locations where chloromethyl methyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) be provided with and required to use clean, full-body CPC (smocks, coveralls, or long-sleeved shirts and long pants), shoe covers, and gloves prior to entering a regulated area; (2) be provided with and required to use approved respirators (a respirator affording higher levels of protection may be substituted); and (3) remove the protective clothing and equipment prior to exiting a regulated area, and at the last exit of the day, place used clothing and equipment in impervious containers for decontamination or disposal.

SANITATION

For closed system operations or in locations where chloromethyl methyl ether is contained in an otherwise "closed system" but is transferred, charged, or discharged into other normally closed containers, OSHA requires that workers: (1) wash their hands, forearms, faces, and necks prior to exiting from the regulated area and before engaging in other activities, and (2) shower after the last exit of the day in designated facilities.

In isolated systems, such as a "glove box," OSHA requires that workers wash their hands and arms with soap and water upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

If it is necessary for workers to wear protective clothing, OSHA requires that a clean change room be provided and equipped with showers and washing facilities. NIOSH recommends that lockers that permit separation of street and work clothes be provided for the worker.

Clothing which is contaminated with chloromethyl methyl ether should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of chloromethyl methyl ether from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of chloromethyl methyl ether's hazardous properties.

Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Decontamination and disposal procedures should be established and implemented to remove chloromethyl methyl ether from materials and equipment. Contaminated material should be removed from regulated areas without further contamination of the facility.

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If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

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OSHA requires that hazardous conditions created by spills or leaks be eliminated and that potentially affected areas be decontaminated prior to the resumption of normal operations.

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2. Ventilate area of spill or leak.
3. For small quantities of liquids containing chloromethyl methyl ether, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing chloromethyl methyl ether may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing chloromethyl methyl ether may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

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Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 2.—Respiratory protection for chloromethyl methyl ether

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

Occupational Health Guideline for 1-Chloro-1-Nitropropane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_3H_5CHClNO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with an unpleasant odor that causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1-chloro-1-nitropropane is 20 parts of 1-chloro-1-nitropropane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 100 milligrams of 1-chloro-1-nitropropane per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for 1-chloro-1-nitropropane from 20 ppm to 2 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1-Chloro-1-nitropropane can affect the body if it is inhaled or if it comes in contact with the eyes. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure of animals has produced severe irritation of the lungs with severe breathing difficulties which may be delayed in onset. Liver, heart, kidney, and blood vessel damage were also reported in animals. In addition, eye irritation has been reported in animals.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1-chloro-1-nitropropane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1-chloro-1-nitropropane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1-chloro-1-nitropropane exposure.

—Chronic respiratory disease: 1-Chloro-1-nitropropane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1-chloro-1-nitropropane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: 1-Chloro-1-nitropropane causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: 1-Chloro-1-nitropropane causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Cardiovascular disease: 1-Chloro-1-nitropropane causes heart damage in animals. In persons with impaired cardiovascular function, the inhalation of 1-chloro-1-nitropropane might cause exacerbation of pre-existing disorders.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1-Chloro-1-nitropropane is a pulmonary irritant and causes liver, kidney, and heart damage in animals. Exposure of rabbits to concentrations near 2600 ppm for

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2 hours was fatal, but 2200 ppm for 1 hour was nonlethal; autopsy revealed pulmonary edema, cellular necrosis of the heart, liver, and kidneys, and cellular damage in the brain. At high concentrations there was lacrimation, nasal discharge, and pulmonary rales. No human experience has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 123.5
  2. Boiling point (760 mm Hg): 140 C (285 F)
  3. Specific gravity (water = 1): 1.2
  4. Vapor density (air = 1 at boiling point of 1-chloro-1-nitropropane): 4.3
  5. Melting point: Data not available
  6. Vapor pressure at 20 C (68 F): 5.8 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.8
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Overheating in closed containers may cause explosions.
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, hydrogen chloride, and carbon monoxide) may be released in a fire involving 1-chloro-1-nitropropane.
  4. Special precautions: Liquid 1-chloro-1-nitropropane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 62 C (144 F) (closed cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: No quantitative information is available concerning the odor threshold of this substance.
  2. Eye Irritation Level: According to the *Handbook of Organic Industrial Solvents*, 1-chloro-1-nitropropane may irritate the eyes.
  3. Evaluation of Warning Properties: Since the TLV has been recommended only to "minimize" irritation, for the purposes of this guideline, 1-chloro-1-nitropropane is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for 1-chloro-1-nitropropane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1-chloro-1-nitropropane.
- Clothing wet with liquid 1-chloro-1-nitropropane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1-chloro-1-nitropropane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1-chloro-1-nitropropane, the person performing the operation should be informed of 1-chloro-1-nitropropane's hazardous properties.
- Non-impervious clothing which becomes wet with liquid 1-chloro-1-nitropropane should be removed promptly and not reworn until the 1-chloro-1-nitropropane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid 1-chloro-1-nitropropane may contact the eyes.

SANITATION

• Skin that becomes wet with liquid 1-chloro-1-nitropropane should be promptly washed or showered with soap or mild detergent and water to remove any 1-chloro-1-nitropropane.
• Eating and smoking should not be permitted in areas where 1-chloro-1-nitropropane is handled, processed, or stored.
• Employees who handle liquid 1-chloro-1-nitropropane should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following partial list includes some common operations in which exposure to 1-chloro-1-nitropropane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent and anti-gelling agent for rubber cements	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.
• **Eye Exposure**
If liquid 1-chloro-1-nitropropane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.
• **Skin Exposure**
If liquid 1-chloro-1-nitropropane gets on the skin, wash the contaminated skin using soap or mild detergent and water. If liquid 1-chloro-1-nitropropane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.
• **Breathing**
If a person breathes in large amounts of 1-chloro-1-nitropropane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
• **Swallowing**
When liquid 1-chloro-1-nitropropane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.
• **Rescue**
Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
• If 1-chloro-1-nitropropane is spilled or leaked, the following steps should be taken:
1. Ventilate area of spill or leak.
2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. Mix spill of up to one gallon with soda ash, spray with water, let stand in bucket with water for two hours, neutralize with dilute hydrochloric acid, flush to sewer, and wash area of spill with detergent and solution.
• Waste disposal methods:
1-Chloro-1-nitropropane may be disposed of:
1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. If quantities of up to one gallon, by the treatment described above.

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RESPIRATORY PROTECTION FOR 1-CHLORO-1-NITROPROPANE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROPENTAFLUOROETHANE

INTRODUCTION

This guideline summarizes pertinent information about chloropentafluoroethane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $CClF_2CF_3$

- **Synonyms**

  F-115; Fluorocarbon-115; Freon 115; Genetron 115; Halocarbon 115; monochloropentafluoroethane

- **Identifiers**

  1. CAS No.: 76-15-3
  2. RTECS No.: KH7877500
  3. DOT UN: 1020 12
  4. DOT label: Nonflammable gas

- **Appearance and odor**

  Chloropentafluoroethane is a colorless, odorless, nonflammable gas; it is shipped as a liquefied gas under its own vapor pressure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 154.47
  2. Boiling point (760 mm Hg): -39.1°C (-38.4°F)
  3. Specific gravity: 5.5 at 20°C (68°F)
  4. Vapor density: Not applicable
  5. Melting point: -106°C (-222.8°F)
  6. Vapor pressure at 21.1°C (69.8°F): 6,034.4 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol and ether
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: Contact of chloropentafluoroethane at high temperatures with alkalies or alka-

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line earth metals such as powdered aluminum, potassium or zinc causes thermal decomposition.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrochloric or hydrofluoric acid, phosgene, fluorides, and chlorides) may be released in a fire involving chloropentafluoroethane.

4. Special precautions: Corrosion can occur when magnesium alloys or aluminum containing more than 2% magnesium is used with fluorocarbon systems in which water may be present.

Flammability

The National Fire Protection Association has not assigned a flammability rating for chloropentafluoroethane; this substance is a nonflammable gas.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical or carbon dioxide to fight fires involving chloropentafluoroethane.

Fires involving chloropentafluoroethane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloropentafluoroethane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloropentafluoroethane. Structural firefighters' protective clothing may provide limited protection against fires involving chloropentafluoroethane.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chloropentafluoroethane [29 CFR 1910.1000, Table Z-1].

- **NIOSH PEL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1,000 ppm (6,320 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloropentafluoroethane a threshold limit value (TLV) of 1,000 ppm (6,320 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of cardiac, skin, CNS, and respiratory effects associated with exposure to chloropentafluoroethane [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloropentafluoroethane can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chloropentafluoroethane affects the heart and respiratory system at very high doses. Early studies in experimental animals showed that inhalation of a chloropentafluoroethane concentration of approximately 200,000 ppm caused confusion, pulmonary irritation, tremors, and, occasionally, coma [NLM 1992]. At a concen-

tration of 190,000 ppm, chloropentafluoroethane caused cessation of respiration (apnea) in rats exposed from 4 to 26 min [NLM 1992]. Rats exposed at 800,000 ppm plus 20% oxygen for 4 hr showed no clinical effects of histopathology. Rats and guinea pigs exposed at 600,000 ppm chloropentafluoroethane in oxygen for 2 hr and guinea pigs exposed at 200,000 ppm chloropentafluoroethane in air for varying intervals up to 2 hr showed no adverse clinical signs [ACGIH 1991]. Studies with anesthetized dogs, rats, and monkeys showed that, under certain conditions, exposures of 100,000 to 200,000 ppm of chloropentafluoroethane may increase blood pressure, accelerate heart rate, cause myocardial depression, or change pulmonary mechanics [ACGIH 1991]. Species differences in sensitivity are great. Monkeys do not show respiratory or circulatory effects when exposed to a 200,000 ppm concentration of chloropentafluoroethane; dogs show no respiratory depression when exposed to 200,000 ppm but do show bronchoconstriction, decreased compliance, sensitization of the heart to epinephrine, tachycardia, myocardial depression, and hypotension when inhaling 100,000 to 250,000 ppm chloropentafluoroethane; rats show bronchospasm, decreased compliance, and respiratory stimulation after inhalation of 100,000 ppm chloropentafluoroethane [Clayton and Clayton 1981; NLM 1992]. Rats, mice, rabbits, and dogs which received 90 exposures, 6 hr daily to 100,000 ppm chloropentafluoroethane showed no adverse effects, and rats, guinea pigs, dogs, and cats exposed to 200,000 ppm chloropentafluoroethane for 3.5 hr/day, 5 days/week for 4 weeks also showed no adverse effects after the cessation of exposure [ACGIH 1991].

2. *Effects on Humans:* In humans, chloropentafluoroethane can affect the heart, central nervous system, and skin. The neurological effects of chlorofluorocarbon exposure were evaluated in 27 refrigeration repair workers and 14 age-matched control workers from a local union of plumbers, pipefitters, and insulation workers. Personal air samples taken on two worker-participants over the course of a typical workshift showed average exposures of 1.4 ppm chlorodifluoromethane and 2.2 ppm chloropentafluoroethane. No peripheral neuropathy was seen among the study subjects, and there was no significant difference in mean nerve conduction velocities between study and reference subjects; however, lightheadedness and palpitations were reported significantly more often by refrigeration repair workers than by controls [NLM 1992]. The defatting effects of fluorocarbons such as chloropentafluoroethane, when in prolonged or repeated contact with the skin, may cause dermatologic problems, and contact of the skin with liquefied chloropentafluoroethane may cause frostbite [Clayton and Clayton 1981; Braker and Mossman 1980].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to chloropentafluoroethane include difficult breathing, dizziness, disorientation, incoordination, narcosis, and nausea or vomiting. Exposure to very high concentrations of this substance may affect the heart, causing irregular heartbeat, which could cause death. Contact of the skin with the evaporating liquid may cause frostbite.

2. *Chronic exposure:* The signs and symptoms of chronic exposure of the skin to chloropentafluoroethane include defatting and dermatitis.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of frostbite, toxicity, or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* If tissue is frozen, seek medical attention ***immediately***. If tissue is not frozen, ***immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids. If irritation, pain, swelling, lacrimation, or photophobia develops, get medical attention as soon as possible.

2. *Skin exposure:* If tissue is frozen, seek medical attention ***immediately;*** do not rub the affected areas or flush them with water. If tissue is not frozen, ***immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloropentafluoroethane and may result in worker exposures to this substance:

—Use as a refrigerant in home appliances, mobile air conditioning units, and retail food refrigeration systems and chillers

—Use as a chemical intermediate

The following methods are effective in controlling worker exposures to chloropentafluoroethane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chloropentafluoroethane, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, cardiovascular system, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloropentafluoroethane at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and

other findings consistent with diseases of the skin, cardiovascular system, or respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloropentafluoroethane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloropentafluoroethane on the skin, cardiovascular system, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloropentafluoroethane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chloropentafluoroethane is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.05 liter/min until a recommended air volume of 2.5 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If liquid chloropentafluoroethane contacts the skin, watch for the development of frostbite. If frostbite occurs, the affected part should be wrapped in woolen material and should then be immersed in warm water until medical help is obtained.

Clothing contaminated with liquid chloropentafluoroethane should be removed immediately, and provisions should be made for safely removing this chemical from these articles.

A worker who handles chloropentafluoroethane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where chloropentafluoroethane is handled, processed, or stored.

STORAGE

Chloropentafluoroethane should be stored in a cool, dry, well-ventilated area in tightly sealed, pressurized containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chloropentafluoroethane should be protected from physical damage and should be stored separately from metals, including aluminum, zinc, and beryllium, heat, sparks, and open flame.

LEAKS

In the event of a leak involving chloropentafluoroethane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the leak.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloropentafluoroethane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloropentafluoroethane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chloropentafluoroethane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chloropentafluoroethane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloropentafluoroethane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with chloropentafluoroethane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chloropentafluoroethane permeation; however, the following materials have been tested against chemically similar materials (Freon 113) and have withstood permeation for periods greater than 8 hr: nitrile rubber and Teflon® . Since specific test data are not available for chloropentafluoroethane, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chloropentafluoroethane.

Safety glasses, goggles, or face shields should be worn during operations in which liquid chloropentafluoroethane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloropentafluoroethane. Contact lenses should not be worn if the potential exists for chloropentafluoroethane exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROPICRIN

INTRODUCTION

This guideline summarizes pertinent information about chloropicrin for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  CCl_3NO_2

- **Synonyms**

  Nitrotrichloromethane, trichloronitromethane, nitrochloroform, Chlor-o-pic, Acquinite, Microlysin, Pic-fume, Profume A, Dolochlor, Larvacide 100

- **Identifiers**

  1. CAS No.: 76-06-2
  2. RTECS No.: PB6300000
  3. DOT UN: 1580 56 (liquid chloropicrin)
  4. DOT label: Poison B

- **Appearance and odor**

  At room temperature, chloropicrin is a noncombustible, oily, colorless liquid with an intense and penetrating odor. The odor threshold reported for chloropicrin is 1.1 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 164.4
  2. Boiling point (760 mm Hg): 112°C (234°F)
  3. Specific gravity (water = 1): 1.66 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chloropicrin): 5.7
  5. Melting point: -64°C (-83°F) (solidifies)
  6. Vapor pressure at 20°C (68°F): 20 mm Hg
  7. Solubility: Nearly insoluble in water; soluble in ether, benzene, absolute alcohol, acetic acid, carbon tetrachloride, acetone, methyl alcohol, and carbon disulfide.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, friction, or strong impact may cause chloropicrin to detonate.
  2. Incompatibilities: Contact of chloropicrin with strong oxidizers may cause fires or explosions. Chloropicrin also reacts violently with aniline in the presence of heat, alcoholic sodium hydroxide, sodium methoxide, and propargyl bromide.

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, chlorine, and carbon monoxide) may be released when chloropicrin is heated to decomposition.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to chloropicrin; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving chloropicrin should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloropicrin may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloropicrin. Chemical protective clothing that is specifically recommended for chloropicrin may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chloropicrin.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chloropicrin is 0.1 ppm (0.7 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.7 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for chloropicrin [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloropicrin a threshold limit value (TLV) of 0.1 ppm (0.67 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of severe eye, skin, and respiratory irritation with chloropicrin exposure [NIOSH 1992]. The ACGIH limit is based on the risk of severe eye and pulmonary effects associated with exposure to chloropicrin [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloropicrin can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Chloropicrin is a severe eye, mucous membrane, and lung irritant; it is particularly injurious to the small and medium-size bronchi. The oral LD_{50} in rats is 250 mg/kg, and the LC_{50} in the same species is 14.4 ppm for 4 hours [NIOSH 1993]. Acute poisoning causes pulmonary congestion, hemorrhage, edema, and tissue infiltration [ACGIH 1991]. Rats inhaling chloropicrin for longer test periods (duration unspecified) developed kidney, liver, and muscle damage [ACGIH 1991]. In mice, exposure to a 9-ppm concentration of chloropicrin in air caused a 50-percent decrease in respiratory rate (with ulceration and necrosis of the respiratory tract lining) and moderate lung damage [Hathaway et al. 1991]. A National Cancer Institute bioassay for carcinogenicity in rats and mice administered chloropicrin by gavage yielded inconclusive results [Clayton

and Clayton 1981]. Chloropicrin is weakly mutagenic in bacterial test systems [Hayes and Laws 1991].

2. *Effects on Humans:* Chloropicrin is a lacrimator and a severe irritant of the respiratory system in humans; it also causes severe skin irritation on contact. Chloropicrin was formerly used as a war gas; the gastrointestinal effects associated with exposure caused it to be called "vomiting gas" [Genium 1990]. Splashed into the eye, chloropicrin has caused corneal edema and liquification of the cornea [NLM 1993]. Exposure to a chloropicrin concentration of 15 ppm cannot be tolerated for more than 1 minute, and exposure to 4 ppm for a few seconds is temporarily disabling because it causes severe eye and respiratory irritation [Hathaway et al. 1991]. Exposure to 0.3 to 0.37 ppm chloropicrin for 3 to 30 seconds causes tearing and eye pain, and this substance is also a severe skin irritant [ACGIH 1991; Clayton and Clayton 1981]. Exposure to a 15-ppm concentration of chloropicrin for a few seconds causes respiratory tract injury [Clayton and Clayton 1981]. In humans, exposure to 119 ppm in air for 30 minutes is lethal; death is caused by pulmonary edema [Hathaway et al. 1991]. Twenty-seven workers in a cellulose factory who were exposed to a high (not further specified) concentration of chloropicrin for 3 minutes developed pneumonitis after 3 to 12 hours of irritating coughing and difficulty in breathing; they subsequently developed pulmonary edema and one died [NLM 1993]. Exposure to chloropicrin apparently increases an individual's susceptibility to chloropicrin intoxication on subsequent exposure [Hathaway et al. 1991; Clayton and Clayton 1981]. Sublethal exposures may cause delayed-onset pulmonary edema, and late deaths may occur from secondary infection [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to chloropicrin include severe pain and tearing of the eyes and corneal burns and opacification; burns and redness of the skin; cough, difficulty breathing, and pulmonary edema; and vertigo, nausea, and vomiting.

2. *Chronic exposure:* The signs and symptoms of repeated exposure to chloropicrin include increased susceptibility to the acute effects of this substance and damage to the lungs. Based on effects seen in animals, chronic exposure to chloropicrin may cause enlarged and tender liver, jaundice, elevated liver enzymes, and pus, blood, or protein in the urine.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of chloropicrin! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chloropicrin or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

—Do *not* permit the victim to drink milk or carbonated beverages!

—Do *not* permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloropicrin and lead to worker exposures to this substance:

—Use as a fumigant on stored grains, cereals, fruits, nuts, vegetables, tobacco, floral crops, lawns, turf, and ornamentals

—Use as a soil fumigant, disinfectant, and sterilizer for the control of fungi, nematodes, and other injurious organisms

—Use as a chemical intermediate in organic synthesis of dyes (methyl violet) and as an oxidizing agent

—Use as an additive to impart a warning odor to odorless fumigants and gases

—Restricted use as a rodenticide and pesticide

—Formerly, use as a tear gas and as a chemical warfare agent

The following methods are effective in controlling worker exposures to chloropicrin, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and con-

trol work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to chloropicrin, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

  A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloropicrin at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system and skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloropicrin exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloropicrin on the respiratory system or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloropicrin.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne chloropicrin is made using a midget fritted glass bubbler containing 10 milliliters of isopropanol. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 120 liters is collected. Analysis is conducted by high performance liquid chromatography with an ultraviolet detector or by gas chromatography using an electron capture detector. The limit of detection for this procedure is not known. This method is described in the OSHA Laboratory In-House Methods File [1989].

PERSONAL HYGIENE

If chloropicrin contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with chloropicrin should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of chloropicrin, particularly its potential to cause severe eye and skin irritation.

A worker who handles chloropicrin should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chloropicrin is handled, processed, or stored.

STORAGE

Chloropicrin should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers of chloropicrin should be protected from physical damage or shock and should be stored separately from strong oxidizers and other incompatible materials. Because containers that formerly contained chloropicrin may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chloropicrin, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Ventilate atmosphere to reduce concentrations.
4. Water spray may be used to reduce vapors.
5. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the chloropicrin for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloropicrin is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloropicrin; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of chloropicrin emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although chloropicrin is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloropicrin exceeds prescribed exposure limits. Respirators

may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets) should be worn to prevent skin contact with chloropicrin. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material has been recommended for use against permeation by chloropicrin and provides protection for periods greater than 8 hours: Responder. Teflon withstands permeation by chloropicrin for greater than 4 hr but less than 8 hr.

If chloropicrin is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chloropicrin might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloropicrin. Contact lenses should not be worn if the potential exists for chloropicrin exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR β-CHLOROPRENE

INTRODUCTION

This guideline summarizes pertinent information about β-chloroprene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- Formula

  C_4H_5Cl

- **Structure**

  $H_2C{=}CClCH{=}CH_2$

- **Synonyms**

  Neoprene; 2-chloro-1,3-butadiene; 2-chlorobutadiene; chloroprene

- **Identifiers**

  1. CAS No.: 126-99-8
  2. RTECS No.: EI9625000
  3. DOT UN: 1991 30
  4. DOT label: Flammable liquid

- **Appearance and odor**

  β-Chloroprene is a flammable, colorless liquid with a sharp, bitter odor. The best estimate of the odor threshold for β-chloroprene is 15 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 88.54
  2. Boiling point (760 mm Hg): 59.4°C (138.9°F)
  3. Specific gravity (water = 1): 0.958 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of β-chloroprene): 3.0
  5. Freezing point: -130 C (-202°F)
  6. Vapor pressure at 20°C (68°F): 188 mm Hg
  7. Solubility: Slightly soluble in water; miscible with ether, acetone, and benzene
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Autoxidation forms an unstable peroxide that catalyzes exothermic polymerization of the monomer.
  2. Incompatibilities: Contact of β-chloroprene with liquid or gaseous fluorine causes a violent reaction.

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3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and hydrogen chloride) may be released in a fire involving β-chloroprene.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) for β-chloroprene.

1. Flash point: -20°C (-4°F)
2. Autoignition temperature: -15.6°C (4°F)
3. Flammable limits in air (% by volume): Lower, 4.0; upper, 20.0
4. Extinguishant: Use alcohol foam, dry chemical, carbon dioxide, or water spray to fight fires involving β-chloroprene.

Fires involving β-chloroprene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of β-chloroprene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving β-chloroprene. Chemical protective clothing that is specifically recommended for β-chloroprene may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving β-chloroprene.

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for β-chloroprene is 25 ppm (90 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for β-chloroprene is 1 ppm (3.6 mg/m^3) as a ceiling limit [NIOSH 1992]. A worker's exposure to β-chloroprene shall at no time exceed this limit. However, β-chloroprene has been designated as a potential occupational carcinogen and exposure should be limited to the lowest feasible concentration.

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned β-chloroprene a threshold limit value (TLV) of 10 ppm (36 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned β-chloroprene a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of lung and skin cancer and reproductive effects associated with exposure to this substance [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to β-chloroprene can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* β-Chloroprene causes eye, skin, and respiratory tract irritation, central nervous system depression, liver damage, and reproductive/developmental effects in experimental animals. Acutely poisoned animals showed inflammation of the eyes and mucous membranes and signs of central nervous system depression before dying of respiratory failure [Hathaway et al. 1991]. The oral LD_{50} is 450 mg/kg in rats and 146 mg/kg in mice [NIOSH 1993]. The lowest lethal concentration in rats is 2,280 ppm for

4 hr [Sax and Lewis 1989]. Rats exposed 6 hr/day, 5 days/week for 4 weeks to a β-chloroprene concentration of 40 ppm showed signs of eye and skin irritation and growth depression; when the concentration was increased to 160 or 625 ppm, the animals showed loss of hair, signs of liver damage, and an increased rate of mortality [Hathaway et al. 1991]. By inhalation, chloroprene caused sterility or impotence in more than 50% of rats and mice exposed for 8 hr to concentrations ranging from 120 to 6,227 ppm (rats) or 12 to 152 ppm (mice) [ACGIH 1991; Hathaway et al. 1991]. Studies of chloroprene's embryotoxicity and teratogenicity have reported conflicting results [ACGIH 1991]. The International Agency for Research on Cancer (IARC) concluded that there was inadequate evidence in experimental animals to classify β-chloroprene's carcinogenicity [IARC 1987].

2. *Effects on Humans:* β-Chloroprene causes eye and skin irritation as well as central nervous system depression and may have reproductive, mutagenic, embryotoxic, and/or carcinogenic effects. In contact with the eyes or skin, chloroprene can cause chemical burns [Hathaway et al. 1991]. One fatality involving a worker exposed for 3 to 4 min to an unspecified chloroprene concentration in an unventilated vessel has been reported [ACGIH 1991; Hathaway et al. 1991]. Exposure to β-chloroprene concentrations ranging from 56 to greater than 334 ppm for a 1-month period was associated with hair loss, personality changes, irritability, extreme fatigue, and unbearable chest pain [Hathaway et al. 1991]. Volunteers exposed to a 973-ppm concentration of chloroprene for 15 min experienced nausea and giddiness; when these subjects performed light exercise during the exposure, they experienced these symptoms within 10 min [ACGIH 1991; Hathaway et al. 1991]. Studies of workers exposed to this substance at concentrations of 5 ppm or less report a significant increase in chromosome aberrations, and reproductive effects have been seen in male workers exposed to 0.28 to 1.94 ppm concentrations of chloroprene [Hathaway et al. 1991]. The wives of these workers also reportedly experienced a threefold excess of miscarriages [Hathaway et al. 1991]. Epidemiological studies of chloroprene-exposed workers have yielded conflicting results in the past; however, a recent study of maintenance workers showed a dose-related increase in the incidence of liver, lung, and lymphatic cancers among these workers [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to β-chloroprene may cause redness and inflammation of the eyes and eyelids, corneal necrosis, skin burns, nausea, dizziness, giddiness, personality changes, headache, irritability, reversible hair loss, insomnia, extreme fatigue, respiratory irritation, and severe chest pains.

2. *Chronic exposure:* Chronic exposure to β-chloroprene may cause effects on spermatogenesis or sperm morphology; increased risk of miscarriage; chromosome aberrations; and cancer of the lung, liver, and lymphatic system.

- **Emergency procedures**

WARNING!

Exposed victims may die!
Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of β-chloroprene! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if β-chloroprene or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The use of β-chloroprene in the manufacturing of neoprene and polychloroprene latex may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to β-chloroprene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to β-chloroprene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, respiratory tract, and central nervous system. Medical mon-

itoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to β-chloroprene at or below the prescribed exposure limit. The examining health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, respiratory tract, or central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to β-chloroprene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of β-chloroprene on the eyes, skin, respiratory tract, or central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for β-chloroprene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne β-chloroprene is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.05 liter/min until a maximum air volume of 8 liters is collected. The sample is then treated with carbon disulfide to extract the β-chloroprene. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.03 mg/sample. This method is described in NIOSH Method No. 1002 [NIOSH 1984].

PERSONAL HYGIENE

If β-chloroprene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with β-chloroprene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of β-chloroprene, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles β-chloroprene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where β-chloroprene or a solution containing β-chloroprene is handled, processed, or stored.

STORAGE

β-Chloroprene should be stored in a cool (less than -15°C (5°F)), dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Chloroprene must be inhibited to prevent hazardous polymerization. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of β-chloroprene should be protected from physical damage and should be stored separately from fluorine, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may

be used to handle β-chloroprene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained β-chloroprene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving β-chloroprene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. For small dry spills, use a clean, nonsparking shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the β-chloroprene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

beta-Chloroprene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of β-chloroprene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or otherwise use 10,000 lb or more of β-chloroprene per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of β-chloroprene emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although β-chloroprene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineer-

ing controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of β-chloroprene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (impervious gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent any skin contact with β-chloroprene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have been tested against permeation by β-chloroprene and have demonstrated protection for periods greater than 8 hr: Viton and polyvinyl alcohol.

If β-chloroprene is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which β-chloroprene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with β-chloroprene. Contact lenses should not be worn if the potential exists for β-chloroprene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROSTYRENE

INTRODUCTION

This guideline summarizes pertinent information about o-chlorostyrene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_8H_7Cl

- **Structure**

  $ClC_6H_4CH{=}CH$

- **Synonyms**

  2-Chlorostyrene; ortho-chlorostyrene

- **Identifiers**

  1. CAS No.: 2039-87-4
  2. RTECS No.: WL4160000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  o-Chlorostyrene is a combustible liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 138.6
  2. Boiling point (760 mm Hg): 188.7°C (371.7°F)
  3. Specific gravity (water = 1): 1.10 at 20°C (68°F)
  4. Vapor density: Data not available
  5. Melting point: -63.15°C (-81.67°F)
  6. Vapor pressure at 25°C (77°F): 0.096 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol ether, acetone, petroleum ether, and acetic acid.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks and open flame
  2. Incompatibilities: None reported
  3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine) may be released in a fire involving o-chlorostyrene.
  4. Special precautions: None reported

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- **Flammability**

The National Fire Protection Association has not assigned a flammability rating for o-chlorostyrene; however, other sources report that this substance is combustible.

1. Flash point: 58.9°C (138°F)
2. Autoignition temperature: Data not available
3. Flammable limits in air: Data not available
4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or foam

Fires involving o-chlorostyrene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorostyrene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for o-chlorostyrene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 50 ppm (285 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 75 ppm (430 mg/m^3) as a STEL [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned o-chlorostyrene a threshold limit value (TLV) of 50 ppm (283 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 75 ppm (425 mg/m^3) for periods not to exceed 15 min [ACGIH 1993].

- **Rationale for limits**

The ACGIH limits are based on the risk of liver, kidney, and narcotic effects associated with exposure to o-chlorostyrene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorostyrene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, o-chlorostyrene is toxic to the liver and kidneys. Applied to rabbit skin for 24 hr, 10 mg of o-chlorostyrene caused irritation [Sax and Lewis 1989]. The dermal LD_{50} in rabbits is 20 g/kg [Sax and Lewis 1989]. The instillation of 500 mg into the eyes of rabbits also caused irritation [Sax and Lewis 1989]. The oral LD_{50} in rats is 5.2 g/kg [Sax and Lewis 1989]. A group of 24 rats, 3 rabbits, 12 guinea pigs, and 1 dog of each sex were exposed 7 hr/day, 5 days/week for a total of 130 exposures in 180 days to an analytically determined average o-chlorostyrene concentration of 101 ppm (576 mg/m^3). No adverse effects on appearance, growth, demeanor, mortality, hematology, or blood chemistry values were apparent; at autopsy, no changes in organ weights or gross pathology were evident. However, microscopic examination of the liver and kidney tissues of animals of all four species showed a slightly higher incidence than in controls of changes in these organs [ACGIH 1991].
2. *Effects on Humans:* No toxic effects of o-chlorostyrene exposure have been reported in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Based on effects seen in animals, contact of the skin or eyes with o-chlorostyrene may cause irritation.
2. *Chronic exposure:* Based on effects seen in animals, long-term exposure to o-chlorostyrene may cause hematuria, proteinuria, acidosis, an enlarged liver, jaundice, and elevated liver enzymes.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of o-chlorostyrene. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorostyrene or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorostyrene and may result in worker exposures to this substance:

—Use in organic synthesis and in the preparation of specialty polymers

The following methods are effective in controlling worker exposures to o-chlorostyrene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveil-

lance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to o-chlorostyrene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver and kidneys.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorostyrene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the liver or kidneys.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorostyrene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorostyrene on the liver or kidneys. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for o-chlorostyrene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorostyrene is determined by using a charcoal tube (100/50-mg sections, 20/40 mesh). STEL and TWA samples are both collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 20 liters (TWA) or 3 liters (STEL) is collected. The sample is then treated with carbon disulfide to extract the o-chlorostyrene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If o-chlorostyrene contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with o-chlorostyrene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of o-chlorostyrene.

A worker who handles o-chlorostyrene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where o-chlorostyrene or a solution containing o-chlorostyrene is handled, processed, or stored.

STORAGE

o-Chlorostyrene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorostyrene should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained o-chlorostyrene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorostyrene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
6. For large liquid spills, call the local fire department.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorostyrene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of o-chlorostyrene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorostyrene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorostyrene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of

o-chlorostyrene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with o-chlorostyrene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to o-chlorostyrene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to o-chlorostyrene.

If o-chlorostyrene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorostyrene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorostyrene. Contact lenses should not be worn if the potential exists for o-chlorostyrene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR o-CHLOROTOLUENE

INTRODUCTION

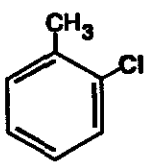
This guideline summarizes pertinent information about o-chlorotoluene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$CH_3C_6H_4Cl$

- **Structure**



- **Synonyms**

2-Chloro-1-methylbenzene; 2-chlorotoluene; 2-methylchlorobenzene; 1-methyl-2-chlorobenzene; *o*-tolyl chloride; Halso 99

- **Identifiers**

1. CAS No.: 95-49-8
2. RTECS No.: XS9000000
3. DOT UN: 2238 27
4. DOT label: Flammable liquid

- **Appearance and odor**

o-Chlorotoluene is a colorless liquid. The odor threshold for o-chlorotoluene is 0.32 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 126.59
2. Boiling point (760 mm Hg): 159°C (318.2°F)
3. Specific gravity (water = 1): 1.083 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of o-chlorotoluene): 4.37
5. Melting point: -35.1°C (-31.18°F)
6. Vapor pressure at 43.2°C (109.8°F): 10 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; freely soluble in alcohol, acetone, ether, benzene, carbon tetrachloride, and chloroform

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of o-chlorotoluene with oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving o-chlorotoluene.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to o-chlorotoluene (unspecified isomer, mixture, or concentration).

1. Flash point: 52°C (126°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, CO_2, water spray, or standard foam to fight fires involving o-chlorotoluene.

Fires involving o-chlorotoluene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of o-chlorotoluene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving o-chlorotoluene. Structural firefighters' protective clothing may provide limited protection against fires involving o-chlorotoluene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for o-chlorotoluene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) as 50 ppm (250 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and 75 ppm (375 mg/m^3) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned o-chlorotoluene a threshold limit value (TLV) of 50 ppm (259 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of moderate skin and eye irritation. The ACGIH limit is based on the risk of eye and skin irritation and systemic poisoning associated with exposure to o-chlorotoluene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to o-chlorotoluene can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

Summary of toxicology

1. *Effects on Animals:* In animals, o-chlorotoluene is irritating to the eyes and skin and, at high doses, this substance affects the central nervous system. A 24-hr patch test with o-chlorotoluene showed moderate skin irritation on both abraded and intact rabbit skin [ACGIH 1991]. Undiluted liquid o-chlorotoluene applied to the skin of guinea pigs under an occlusive dressing in doses of 1 ml/kg or 10 ml/kg for a 24-hr period caused moderately severe local irritation and evidence of skin absorption [ACGIH 1991]. One drop of undiluted o-chlorotoluene instilled into the eye of a rabbit resulted in moderate conjunctival erythema; the cornea was opaque 24 hr after instillation but appeared normal 2 weeks later [ACGIH 1991]. The oral LD_{50} in rats is 5,700 mg/kg, and three of 20 rats died after inhaling approximately 2,400 ppm [EPA 1989]. Rats exposed by inhalation for 6 hr to a 4,000-ppm concentration of o-chlorotoluene lost coordination in 1.5 hr, became prostrate after 1.75 hr, and showed tremors after 2 hr of exposure; marked vasodilation also developed in these animals. All three rats survived, however, and had gained weight (averaging 33 grams) 2 weeks later. Mice, rats, and guinea pigs exposed at a chamber concentration of 4,400 ppm exhibited the following: gasping, ataxia, and convulsions in mice within 30 min after exposure, and gasping, hyperpnea, ataxia, and convulsions in rats and guinea pigs in 45 min. All animals were comatose in 60 min. All mice and rats died as did 7 of 10 guinea pigs. Two guinea pigs were alive 2 week postexposure [ACGIH 1991]. Three rats exposed to 14,000 ppm o-chlorotoluene survived but showed loss of coordination, vasodilation, labored respiration, and narcosis. Of three rats exposed to 175,000 ppm, two were severely incapacitated while the other died. The two that survived were gaining weight 2 weeks later [ACGIH 1991].

2. *Effects on Humans:* There are no reports of the effects of exposure to o-chlorotoluene in humans.

Signs and symptoms of exposure

1. *Acute exposure:* Based on effects seen in animals, acute overexposure to o-chlorotoluene may cause dizziness; loss of coordination; tremors; difficult breathing; redness, inflammation, and tearing of the eyes; and redness and inflammation of the skin.

2. *Chronic exposure:* No signs or symptoms of continued low-level exposure to o-chlorotoluene have been reported.

Emergency procedures

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of o-chlorotoluene! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if o-chlorotoluene or any material containing it is ingested:

—Do ***not*** induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve o-chlorotoluene and may result in worker exposures to this substance:

—Use as a solvent and as an intermediate in the production of organic chemicals, pharmaceuticals, synthetic rubber compounds, and dyes

—Use as an intermediate in the production of herbicides

The following methods are effective in controlling worker exposures to o-chlorotoluene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

— Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

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Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to o-chlorotoluene, the licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and central nervous system.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to o-chlorotoluene at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, or central nervous system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to o-chlorotoluene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of o-chlorotoluene on the eyes, skin, or central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for o-chlorotoluene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne o-chlorotoluene is determined by using a charcoal tube (100/150-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 20 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is an OSHA modification of NIOSH Method 1003, *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If o-chlorotoluene contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with o-chlorotoluene should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of o-chlorotoluene, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles o-chlorotoluene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where o-chlorotoluene is handled, processed, or stored.

STORAGE

o-Chlorotoluene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of o-chlorotoluene should be protected from physical damage and should be stored separately from oxidizing materials, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained o-chlorotoluene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving o-chlorotoluene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and gently place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the o-chlorotoluene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  o-Chlorotoluene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR Part 355.40] to notify the National Response Center of an accidental release of o-chlorotoluene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of o-chlorotoluene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although o-chlorotoluene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of o-chlorotoluene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves and other protective clothing, as appropriate) should be worn to prevent any skin contact with o-chlorotoluene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Viton® may withstand permeation by o-chlorotoluene for more than 4 but fewer than 8 hr. The following materials have breakthrough times of less than 1 hr and are not recommended for use with o-chlorotoluene: butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl chloride, and Saranex.

If o-chlorotoluene is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which o-chlorotoluene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with o-chlorotoluene.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

EPA [1989]. Drinking water health advisory: o-Chlorotoluene. Washington, D.C.: U.S. Environmental Protection Agency, Office of Drinking Water.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-CHLORO-6-TRICHLOROMETHYL PYRIDINE

INTRODUCTION

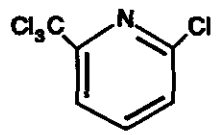
This guideline summarizes pertinent information about 2-chloro-6-trichloromethyl pyridine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_6H_3Cl_4N$

- **Structure**



- **Synonyms**

  Nitrapyrin; α,α,α-6-tetrachloro-2-picoline; N-Serve, N-Serve nitrogen stabilizer; Dowco-163

- **Identifiers:**

  1. CAS No.: 1929-82-4
  2. RTECS No.: US7525000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  2-Chloro-6-trichloromethyl pyridine is a colorless or white, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 230.93
  2. Boiling point (11 mm Hg): 136°–137.5°C (276.8°–279.5°F)
  3. Specific gravity (water = 1): Data not available
  4. Vapor density: Not applicable
  5. Melting point: 62.5°–62.9°C (144.5°–145.2°F)
  6. Vapor pressure: 0.0028 mm Hg at 23°C (73.4°F)
  7. Solubility: Insoluble in water
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Aluminum, magnesium, or their alloys

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen) may be released in a fire involving 2-chloro-6-trichloromethyl pyridine.

4. Special precautions: None

Flammability

The National Fire Protection Association has not assigned a flammability rating for 2-chloro-6-trichloromethyl pyridine.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving boron oxide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2-chloro-6-trichloromethyl pyridine.

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) for 2-chloro-6-trichloromethyl pyridine are 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limits (RELs) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 20 mg/m^3. The STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-chloro-6-trichloromethyl pyridine a threshold limit value (TLV) of 10 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 20 mg/m^3 for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 min [ACGIH 1991].

Rationale for limits

The OSHA limits are based on the risk of physical irritation associated with exposure to 2-chloro-6-trichloromethyl pyridine [54 Fed. Reg. 2592 (1989)].

HEALTH HAZARD INFORMATION

Routes of exposure

Exposure to 2-chloro-6-trichloromethyl pyridine can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

Summary of toxicology

1. *Effects on Animals:* In animals, 2-chloro-6-trichloromethyl pyridine is moderately toxic when ingested or absorbed through the skin. The dermal LD_{50} in rabbits is 850 mg/kg [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50}s in rats, mice, and rabbits are 940 mg/kg, 710 mg/kg, and 500 mg/kg respectively [NIOSH 1993; Sax and Lewis 1989]. Dogs and rats fed 15 mg/kg 2-chloro-6-trichloromethyl pyridine daily for 93 days showed no adverse effects on behavior, growth, food consumption, body and organ weights, mortality, or serum chemistries; at autopsy, no gross or microscopic changes to the organs or tissues were detectable [ACGIH 1991]. Male rats fed concentrations of 1,000 ppm in the diet for 2 years had a statistically significant reduction in mean body weight at 12 months, but not at 18 and 24 months. No effects were recorded at lower concentrations. Female rats fed between 30 and 1,000 ppm for 2 years had an increased incidence of bile duct hyperplasia [Dow Chemical USA 1967].

2, *Effects on Humans:* There are no data on the acute or chronic effects of exposure to 2-chloro-6-trichloromethyl pyridine in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to 2chloro-6-trichloromethyl pyridine may irritate the eyes, nose, throat, and skin. Higher levels may cause dizziness and lightheadness.

2. *Chronic exposure:* Chronic exposure to 2-chloro-6-trichloromethyl pyridine may cause dizziness, headaches, loss of appetite and insomnia. Repeated exposure may affect the liver and kidneys.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 2-chloro-6-trichloromethyl pyridine or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve 2-chloro-6-trichloromethyl pyridine and result in worker exposures to this substance:

—Use as a fertilizer additive to control nitrification and prevent loss of soil nitrogen from land to be planted with corn, cotton, wheat, or sorghum

—Manufacture, formulation, and application of 2-chloro-6-trichloromethyl pyridine-containing products

Methods that are effective in controlling worker exposures to 2-chloro-6-trichloromethyl pyridine, depending on the feasibility of implementation, are:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH:

American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-chloro-6-trichloromethyl pyridine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the kidneys, liver, eyes, and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-chloro-6-trichloromethyl pyridine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) including a history and other findings consistent with diseases of the kidneys, liver, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-chloro-6-trichloromethyl pyridine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-chloro-6-trichloromethyl pyridine on the kidneys, liver, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2-chloro-6-trichloromethyl pyridine.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

The OSHA method for determining worker exposure to airborne concentrations of 2-chloro-6-trichloromethyl

pyridine (total dust) is made using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Particulates not otherwise regulated (Total Dust) [OSHA 1987].

The OSHA method for determining worker exposure to airborne concentrations of 2-chloro-6-trichloromethyl pyridine (respirable fraction) is made using a tared, low-ash polyvinyl chloride filter with a 5-micron pore size; the filter is contained in a 37-mm cassette. Air is drawn through the filter cassette, which is preceded by a 10-mm nylon cyclone, at a flow rate of 1.7 liter/min until a maximum air volume of 816 liters is collected. Analysis is conducted by gravimetric measurement (weighing) of the filter. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Chemical Information Manual* as Particulates not otherwise regulated (Respirable Fraction) [OSHA 1987].

PERSONAL HYGIENE

If 2-chloro-6-trichloromethyl pyridine contacts the skin, workers should wash the skin with soap and water.

Clothing contaminated with 2-chloro-6-trichloromethyl pyridine should be removed.

A worker who handles 2-chloro-6-trichloromethyl pyridine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or apply cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 2-chloro-6-trichloromethyl pyridine or a solution containing 2-chloro-6-trichloromethyl pyridine is handled, processed, or stored.

STORAGE

2-Chloro-6-trichloromethyl pyridine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. This substance should not be stored in unlined containers or be pumped with equipment made of aluminum, magnesium, or alloys of these metals. Containers of 2-chloro-6-trichloromethyl pyridine should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-chloro-6-trichloromethyl pyridine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. No specific information is available on clean-up procedures for spills or leaks involving this substance.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  2-Chloro-6-trichloromethyl pyridine is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 CFR 355.40] to notify the National Response Center of an accidental release of 2-chloro-6-trichloromethyl pyridine; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of 2-chloro-6-trichloromethyl pyridine emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-

261.24. Although 2-chloro-6-trichloromethyl pyridine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-chloro-6-trichloromethyl pyridine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent prolonged or repeated skin contact with 2-chloro-6trichloromethyl pyridine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2-chloro-6-trichloromethyl pyridine. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2-chloro-6-trichloromethyl pyridine.

If 2-chloro-6-trichloromethyl pyridine is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-chloro-6-trichloromethyl pyridine might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-chloro-6-trichloromethyl pyridine. Contact lenses should not be worn if the potential exists for 2-chloro-6-trichloromethyl pryidine exposure.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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Government Printing Office, Office of the Federal Register.

Dow Chemical USA [1967]. Chronic toxicity study of nitrapyrin. Cited in U.S. Environmental Protection Agency, MRID Nos. 000375531 and 000375532. Washington, DC: U.S. Environmental Protection Agency.

54 Fed. Reg. 2592 [1989]. Occupational Safety and Health Administration: air contaminants, final rule (29 CFR 1910).

NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

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Sax NI, Lewis RJ [1989]. Dangerous properties of industrial materials. 7th ed. New York, NY: Van Nostrand Reinhold Company.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLORPYRIFOS

INTRODUCTION

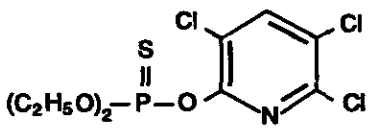
This guideline summarizes pertinent information about chlorpyrifos for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_9H_{11}Cl_3NO_3PS$

- **Structure**



- **Synonyms**

Brodan; chloropyrifos-ethyl; O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate; DOWCO 179; Dursban; Lorsban; Pyrinex

- **Identifiers**

1. CAS No.: 2921-88-2
2. RTECS No.: TF6300000
3. DOT UN: 2783 55
4. DOT label: None

- **Appearance and odor**

Chlorpyrifos is a colorless to white, crystalline solid with a mild, mercaptan-like odor. The technical grade often contains volatile contaminants, which are partly responsible for the offensive odor of this substance. Chlorpyrifos is an organophosphate insecticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 350.57
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.398 at 43.5°C (110.3°F) (liquid)
4. Vapor density: Data not available
5. Melting point: 41° to 42°C (105.8° to 107.6°F)
6. Vapor pressure at 25°C (77°F): 0.00002 mm Hg
7. Solubility: Slightly soluble in water; soluble in most organic solvents; slowly hydrolyzed by acid or alkaline solutions
8. Evaporation rate: Data not available

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Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of chlorpyrifos with strong acids (such as hydrochloric, sulfuric, or nitric acid) causes a violent reaction. Contact with acidic or alkaline solutions causes hydrolysis.

3. Hazardous decomposition products: Toxic gases (such as chlorine and the oxides of nitrogen, phosphorus, and sulfur) may be released in a fire involving chlorpyrifos.

4. Special precautions: Chlorpyrifos is corrosive to copper and brass.

Flammability

The National Fire Protection Association has not assigned a flammability rating to chlorpyrifos; however, this substance is combustible.

1. Flash point: 27.8°C (82°F)(Dursban®); 30.6°C (87°F)(Lorsban)(TAG closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving chlorpyrifos.

Fires involving chlorpyrifos should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chlorpyrifos may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Do not scatter this material. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorpyrifos. Chemical protective clothing that is specifically recommended for chlorpyrifos may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chlorpyrifos.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chlorpyrifos [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.2 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.6 mg/m^3 as a short-term exposure limit (STEL). The STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday. The NIOSH REL also bears a Skin notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorpyrifos a threshold limit value (TLV) of 0.2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to chlorpyrifos [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to chlorpyrifos.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorpyrifos can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, chlorpyrifos is an inhibitor of blood and plasma cholinesterase. The dermal LD_{50} in rabbits is 2,000 mg/kg, and the oral LD_{50} in rats is 82 mg/kg [NIOSH 1990]. Administered to monkeys at doses of 2.0 or 0.4 mg/kg/day for

6 months (route not specified), chlorpyrifos caused inhibition of plasma and red blood cell cholinesterase; at a dose of 0.08 mg/kg/day, only the plasma enzyme was inhibited in these animals [Hayes 1982]. Brain cholinesterase was not affected at any of these doses, and no clinical or morphological effects were noted at autopsy [Hayes 1982]. In 2-year feeding studies in dogs and rats, doses of 1 or 3 mg/kg/day produced depression of plasma and red blood cell cholinesterase; brain cholinesterase was depressed only at the highest dose [Hayes 1982]. In both rats and dogs, even the highest dose (3 mg/kg/day) produced no clinically important effects, as judged by survival, growth, relative and absolute organ weights, blood, urine, and clinical chemical findings, and gross and microscopic pathology [Hayes 1982]. In a three-generation reproduction and fertility study, no teratologic or reproductive effects were seen in male and female rats fed 1 mg/kg/day chlorpyrifos [ACGIH 1991].

2. *Effects on Humans:* In humans, chlorpyrifos is an inhibitor of plasma cholinesterase. The lowest toxic dose in humans is estimated to be 300 mg/kg; this dose caused peripheral nervous system effects, muscular weakness, and coma [NIOSH 1990]. Four repeated chlorpyrifos doses (10 mg/kg each) were applied to the skin of volunteers for a 24-hr period (each application) and caused no plasma cholinesterase depression; however, increasing the dose to 25 mg/kg did produce plasma cholinesterase inhibition, even when the duration of skin contact was reduced to 12 hr [ACGIH 1991]. Human male volunteers given 0.014 or 0.03-mg/kg chlorpyrifos per day for 20 days, followed by 0.1 mg/kg/day for an additional 9 days, showed no adverse behavioral effects or changes in hematology, urinalysis, or biochemistry parameters [Hayes 1982]. At the highest dose, plasma cholinesterase was depressed in these volunteers, but cholinesterase levels returned to normal within 4 weeks of the cessation of exposure. Red blood cell cholinesterase activity was not affected at any level [Hayes 1982]. Five of seven workers applying chlorpyrifos spray with hand-operated power sprayers (0.5% emulsion or 0.25% or 0.5% suspensions of water-wettable powder) had plasma cholinesterase values that were more than 50% below baseline values within 2 weeks after beginning work, and one worker had a plasma enzyme reduction that was greater than 70%. No inhibition of red blood cell cholinesterase was observed in these workers, and there were no signs or symptoms of illness [Hayes 1982; ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to chlorpyrifos depends on the route and extent of exposure. Inhalation can cause respiratory and ocular effects, often within a few minutes of exposure, and may cause a feeling of tightness in the chest, wheezing, laryngeal spasms, excessive salivation, bluish/purplish discoloration of the skin and lips, narrowed pupils, blurred vision, tearing, runny nose, or frontal headache. Ingestion of chlorpyrifos may cause anorexia, nausea, vomiting, abdominal cramps, and diarrhea. Skin absorption may result in localized sweating and muscle tremors in the area where skin absorption took place.

2. *Chronic exposure:* Repeated exposure to concentrations of chlorpyrifos too low to cause signs or symptoms after a single exposure may produce the signs and symptoms of poisoning described above. Continued daily exposure to low doses of chlorpyrifos may cause increasingly severe effects.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical con-

tamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chlorpyrifos or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chlorpyrifos and may result in worker exposures to this substance:

—Manufacture, formulation, and application of pesticides containing chlorpyrifos

—Use as an acaricide

—Use as an agricultural insecticide on corn, deciduous fruits and nuts, alfalfa, cotton, sorghum, and citrus crops and as a nonagricultural pesticide for household pests and aquatic larvae

—Use in controlling chinch bugs in Gulf Coast states and in controlling ticks on cattle and sheep in Australia

The following methods are effective in controlling worker exposures to chlorpyrifos, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to chlorpyrifos, a licensed health care professional should evaluate and document the worker's base-

line health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood (plasma and red blood cell cholinesterase levels).

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chlorpyrifos at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the blood. Pre-exposure baseline plasma and red blood cell cholinesterase levels should be established.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorpyrifos exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorpyrifos on plasma or red blood cell cholinesterase activity levels. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophosphorus compounds such as chlorpyrifos. RBC ChE is an indicator of both acute and chronic overexposure. The recommended biological exposure index for chlorpyrifos (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for preexposure and exposure measurements to reduce variability.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorpyrifos is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.05 and is found in OSHA Method No. 62 in the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

If chlorpyrifos contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with chlorpyrifos should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chlorpyrifos, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles chlorpyrifos should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chlorpyrifos or a solution containing chlorpyrifos is handled, processed, or stored.

STORAGE

Chlorpyrifos should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accor-

dance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chlorpyrifos should be protected from physical damage and should be stored separately from strong acids (such as hydrochloric, sulfuric, or nitric acid), heat, sparks, and open flame. Because containers that formerly contained chlorpyrifos may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorpyrifos, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Use water spray to reduce vapors.

6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

7. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the chlorpyrifos for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Chlorpyrifos is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for chlorpyrifos is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorpyrifos emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chlorpyrifos is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation,

EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorpyrifos exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should only use respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with chlorpyrifos. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chlorpyrifos permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have demonstrated good resistance: laminates of Viton and neoprene or of butyl rubber and neoprene. Since specific test data are not available for chlorpyrifos, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chlorpyrifos.

If chlorpyrifos is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chlorpyrifos might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chlorpyrifos. Contact lenses should not be worn if the potential exists for chlorpyrifos exposure.

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Occupational Health Guideline for Chromic Acid and Chromates*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all chromic acid and chromates. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Chromic acid

- Formula: CrO_3
- Synonyms: Chromic anhydride; chromium trioxide
- Appearance and odor: Dark red, deliquescent, odorless solid.

Sodium dichromate

- Formula: $Na_2Cr_2O_7$-$2H_2O$
- Synonyms: Sodium bichromate (dihydrate)
- Appearance and odor: Red-orange, odorless solid.

Potassium chromate

- Formula: K_2CrO_4
- Synonyms: Chromate of potash
- Appearance and odor: Yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chromic acid or chromates is a ceiling of 0.1 milligram of chromic acid or chromates per cubic meter of air (mg/m³). Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: The non-carcinogenic forms include the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to 0.001 Cr (VI) mg/m³ and that thesecompounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to 0.025 Cr (VI) mg/m³ averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.05 Cr (VI) mg/m³ averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chromic acid or chromates can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Chromic acid mist and chromate dusts may cause severe irritation of the nose, throat, bronchial tubes, and lungs. Chromic acid splashed in the eyes may cause severe injury. If swallowed, chromates and sodium and potassium dichromates may cause stomach and kidney problems. These

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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compounds, if swallowed, often cause vomiting. Skin exposure to chromic acid or chromates may cause ulceration of the skin.

2. Long-term Exposure: Repeated or prolonged exposure to chromic acid or chromate dust or mist may cause an ulceration and perforation of the nasal septum. Respiratory irritation may occur with symptoms resembling asthma. Liver damage with yellow jaundice has been reported. Prolonged or repeated exposure of the skin may cause a skin rash. Allergic skin rash may also occur. An increased amount of lung cancer has been found in employees in the chromate-producing industry.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chromic acid or chromates.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chromic acid or chromates at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to chromic acid or chromates would be expected to be at increased risk from exposure. Examination of the respiratory system, blood, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Chromates have been shown to cause blood changes in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—14" x 17" chest roentgenogram: Chromates may cause human lung damage and are associated with a high incidence of lung cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chromates are reported to cause decreased pulmonary function. Periodic surveillance is indicated.

—Urinalysis: Since chromates may cause kidney damage, a urinalysis should be obtained, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Chromates may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Chromates are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Emphasis should be placed on observation for changes in the mucous membranes of the upper respiratory tract, ulceration of the skin, and surveillance for malignancy of the respiratory tract and lungs.

• **Summary of toxicology**

Chromic acid mist and chromate dusts are severe irritants of the nasopharynx, larynx, lungs, and skin. Chromium compounds, especially the hexavalent compounds are associated with a high incidence of lung cancer in humans. Administered subcutaneously to rabbits and guinea pigs, chromates produce kidney damage, with albuminuria and cylindruria; fatal nephritis occurred in a human treated with chromic acid to cauterize a wound. Workers exposed to chromic acid or chromates in concentrations of 0.11 to 0.15 mg/m^3 developed ulcers of the nasal septum and irritation of the conjunctiva, pharynx and larynx, as well as asthmatic bronchitis. A worker exposed to unmeasured but massive amounts of chromic acid mist for 4 days developed severe frontal headache, wheezing, dyspnea, cough, and pain on inspiration; after 6 months there was still chest pain on inspiration and cough. In an industrial plant where the airborne chromic acid concentrations measured from 0.18 to 1.4 mg/m^3, moderate irritation of the nasal septum and turbinates was observed after 2 weeks of exposure, ulceration of the septum after 4 weeks, and perforation of the septum after 8 weeks. A worker exposed to an unmeasured concentration of chromic acid mist for 5 years developed jaundice and was found to be excreting significant amounts of chromium; liver function in four other workers with high urinary chromium excretion was mildly to moderately impaired. Other studies of chromate workers have not found any unusual incidence of liver diseases or other systemic diseases except for lung cancer. Erosion and discoloration of the teeth has been attributed to chromic acid exposure. Blood changes were observed in chromate plant workers, including leukocytosis or leukopenia, monocytosis, and eosinophilia. A markedly increased incidence of bronchogenic carcinoma occurs in workers exposed to chromate dust. The latent period is relatively short, suggesting the presence of a potent carcinogen. Calcium chromate and zinc chromate have been demonstrated to be carcinogenic in rats, and the risk of lung cancer is reportedly increased in chrome pigment workers. Papillomata of the oral cavity and larynx were found in 15 of 77 chrome platers exposed for an average of 6.6 years to chromic acid mist at air concentrations of chromium of 0.4 mg/m^3. There is no positive evidence that chromic acid in the workplace has contributed to an increase in lung cancer, neither is there definitive evidence that absolves chromic acid. A concentrated solution of chromic acid in the eye causes severe corneal injury; chronic exposure to the mist causes conjunctivitis. Chrome ulcer, a penetrating lesion of the skin, occurs chiefly on the hands and forearms where there has been a break in the epidermis; it is believed to be due to a direct necrotizing effect of the chromate ion. The ulcer is relatively painless, heals slowly, and produces a characteristic depressed scar.

Prolonged exposure to chromic acid mist causes dermatitis, which varies from a dry erythematous eruption to a weeping eczematous condition. Cutaneous sensitization to chromate compounds is a common problem in industrial practice.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Chromic acid**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): Decomposes when it melts
3. Specific gravity (water = 1): 2.7
4. Vapor density (air = 1 at boiling point of chromic acid): Not applicable
5. Melting point: 197 C (387 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Data not available (very low)
7. Solubility in water, g/100 g water at 20 C (68 F): 63
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Sodium dichromate**

1. Molecular weight: 298
2. Boiling point (760 mm Hg): 400 C (752 F) (decomposes)
3. Specific gravity (water = 1): 2.34
4. Vapor density (air = 1 at boiling point of sodium dichromate): Not applicable
5. Melting point: 357 C (674 F) (loses water at 85 C (185 F))
6. Vapor pressure at 20 C (68 F): Zero (except for water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 236
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Potassium chromate**

1. Molecular weight: 194
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 2.7
4. Vapor density (air = 1 at boiling point of potassium chromate): Not applicable
5. Melting point: 971 C (1780 F)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 39
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity—Chromic acid or chromates**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with any combustible, organic, or other readily oxidizable materials such as paper, wood, sulfur, aluminum, plastics, etc. may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: Chromic acid or chromates will attack most forms of metals, cloth, leather, plastics, rubber, and coatings and may cause spontaneous ignition.

- **Flammability**

1. Chromic acid is not combustible in itself, but is a powerful, oxidizing material. It will ignite on contact with acetic acid and alcohol.

- **Warning properties**

Grant states that "contact with the solid material or with concentrated solution (of chromic acid) by splash in the eye causes severe corneal injury characterized by infiltration, vascularization, and opacification of the cornea.

"More commonly, exposure to chromic acid occurs in less serious form as a result of spraying of fine droplets into the air from electroplating baths or by transfer to the eyes on the fingers. After chronic exposure to such conditions, the ocular changes seen are chronic conjunctival inflammation, analogous to the well-known irritation of the nasal mucosa which leads to perforation of the nasal septum." In addition, Grant states that "dichromates (bichromates) as ammonium, sodium, or potassium salts are water-soluble, crystalline substances which have a peculiar injurious effect on the cornea, causing great swelling of the corneal stroma."

The *Documentation of TLV's* states that "Vigliani and Zurlo reported . . . irritation of the mucous membranes of the larynx, pharynx, and conjunctiva . . . in a group of workers allegedly exposed to chromates or chromic acid in concentrations ranging from 0.11 to 0.15 mg/m^3."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chromic acid or chromates. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of chromic acid or chromates on a filter, followed by chemical treatment and colorimetric analysis. An analytical method for chromic acid and chromates is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental

concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solids or liquids containing chromic acid or chromates.
- If employees' clothing may have become contaminated with solids or liquids containing chromic acid or chromates, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with chromic acid or chromates should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of substance from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chromic acid or chromates, the person performing the operation should be informed of chromic acid or chromates' hazardous properties.
- Where there is any possibility of exposure of an employee's body to solids or liquids containing chromic acid or chromates, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with chromic acid or chromates should be removed immediately and not reworn until the substance is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solids or liquids containing chromic acid or chromates contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solids or liquids containing chromic acid or chromates, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with chromic acid or chromates should be immediately washed or showered with soap or mild detergent and water to remove any such sbustance.
- Workers subject to skin contact with solids or liquids containing chromic acid or chromates should wash with soap or mild detergent and water any areas of the body which may have contacted such a substance at the end of each work day.
- Eating and smoking should not be permitted in areas where solids or liquids containing chromic acid or chromates are handled, processed, or stored.
- Employees who handle solids or liquids containing chromic acid or chromates should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Areas in which exposure to a carcinogenic form of chromium (VI) may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized personnel only.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chromic acid or chromates may occur and control methods which may be effective in each case:

Operation	Controls
Use in metal finishing in chrome plating, anodizing, conversion coatings, and for corrossion resistance	Local exhaust ventilation; personal protective equipment
Use in leather finishing for shoe uppers, glove and garment leathers, and bag leather	Local exhaust ventilation; personal protective equipment
Use as corrosion inhibitors in radiator coolants, internal combustion and gas turbine engines, refrigerator and air conditioning systems, and water-cooled nuclear reactors	Local exhaust ventilation; personal protective equipment
Use in photoreproduction processes as sensitizing agents for photoengraving, photography, lithography, and blueprinting	Local exhaust ventilation; personal protective equipment

Operation	Controls
Use as corrosion-inhibiting and coloring pigments, artists' colors, jointing pastes, inks, rubber, and ceramics, and color blending	Process enclosure; local exhaust ventilation; personal protective equipment
Use in dyeing of fur, leather, fabrics, wool, and nylon; oxidizing of dyes; aftertreating on cotton, and in textile and paper printing; use in manufacture of glue used in shoes, furniture, and packaging	Local exhaust ventilation; personal protective equipment
Use as fungicides; use in aqueous preservatives and fire retardants for wood; for protection of textiles and seed	Local exhaust ventilation; personal protective equipment
Use in battery manufacture to increase shelf life; to provide corrosion resistance and for battery depolarization	Local exhaust ventilation; personal protective equipment
Use in manufacture of safety matches and explosives	Local exhaust ventilation; personal protective equipment
Use as a chemical reagent, oxidizing agent, catalyst, indicator, in bleaching of fats, oils, and waxes, in chemical synthesis, and in analytical chemistry	Local exhaust ventilation; personal protective equipment
Use in manufacture and packaging of cement	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If solids or liquids containing chromic acid or chromates get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

• **Skin Exposure**

If solids or liquids containing chromic acid get on the skin, immediately flush the contaminated skin with soap or mild detergent and water. If chromic acid soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If chromates get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing chromic acid or chromates penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of chromic acid or chromates, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When solids or liquids containing chromic acid or chromates have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If chromic acid or chromates are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing chromic acid or chromates should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Chromic acid or chromates may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.
• **Warning properties**

RESPIRATORY PROTECTION FOR CHROMIC ACID AND CHROMATES

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
30 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 30 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Soluble Chromic and Chromous Salts (as Chromium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble chromic and chromous salts. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Chromic sulfate hydrate

- Formula: $Cr_2(SO_4)_3$-$16H_2O$ (approximately)
- Synonyms: None
- Appearance and odor: Violet or green, odorless solid.

Chromic potassium sulfate

- Formula: $KCr(SO_4)_2$-$12H_2O$
- Synonyms: Potassium chrome alum; potassium chromium (III) sulfate
- Appearance and odor: Red-violet, odorless solid.

Chromous chloride

- Formula: $CrCl_2$
- Synonyms: None
- Appearance and odor: Colorless to gray, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble chromic or chromous salts is 0.5 milligrams of soluble chromic or chromous salts (as chromium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: They are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to 0.001 mg/m^3 and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to 0.025 Cr (VI) mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.05 Cr (VI) mg/m^3 averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble chromic or chromous salts can affect the body if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Exposure to certain soluble chromic or chromous salts have been reported to cause an allergic skin rash.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble chromic or chromous salts.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble chromic and chromous salts at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble chromic and chromous salts exposure.

—Skin disease: Chromic salts may cause an allergic dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

• **Summary of toxicology**

The soluble chromic and chromous salts have no established toxicity. Since exposures are often mixed, consideration should be given to the possible exposure to hexavalent chromium, which is a more toxic form. The compound hexaaquachromium trichloride has been found to react with protein in vitro, indicating that it is not biologically inert. Of 35 rats implanted with chromic acetate in the thigh muscle, 1 developed sarcoma; this was considered to be evidence of weak carcinogenicity of this soluble trivalent compound. When taken by mouth, the trivalent compounds do not give rise to local or systemic effects and are poorly absorbed; no specific effects are known to result from inhalation. Animals ingesting chromic salts showed one-ninth as much chromium in the tissues as did animals ingesting equal amounts of chromates. Dermatitis from some chromic salts has been reported. Some investigators believe that all persons sensitized to hexavalent chromium are also sensitive to the trivalent form, although this has not been firmly established.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Chromic sulfate hydrate**

1. Molecular weight: 680 (approximately)
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of chromic sulfate hydrate): Not applicable
5. Melting point: 90 C (194 F) Loses water, residue does not melt
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 84— 120
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Chromic potassium sulfate**

1. Molecular weight: 499.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.83
4. Vapor density (air = 1 at boiling point of chromic potassium sulfate): Not applicable
5. Melting point: 89 C (192 F) Loses water, then melts at 400 C (752 F)
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 19.6
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Chromous chloride**

1. Molecular weight: 122.9
2. Boiling point (760 mm Hg): 1300 C (2372 F)
3. Specific gravity (water = 1): 2.93
4. Vapor density (air = 1 at boiling point of chromous chloride): Not applicable
5. Melting point: 820 C (1508 F)
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Water (chromyl chloride)
3. Hazardous decomposition products: None
4. Special precautions: None

• **Flammability**

1. Most soluble chromic or chromous salts are not combustible. However, chromyl chloride reacts vigorously with water, forming chromic acid, chromic chloride, hydrochloric acid, and chlorine. Also, chromyl chloride causes ignition of ammonia, ethyl alcohol, turpentine, and other combustible materials.

• **Warning properties**

Grant states that "chromium compounds . . . are known to cause dermatitis, ulcers of the skin and mucous membranes, and perforation of the nasal septum." Chromium chloride is an example of the chromium compounds which Grant states produces these effects. Not all chromic and chromous salts produce eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of soluble chromic or chro-

mous salts. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of soluble chromic or chromous salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for soluble chromic and chromous salts is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquids or solids containing soluble chromic or chromous salts.

• Clothing contaminated with soluble chromic or chromous salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chromic or chromous salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chromic or chromous salts, the person performing the operation should be informed of soluble chromic or chromous salts's hazardous properties.

• Non-impervious clothing which becomes contaminated with soluble chromic or chromous salts should be removed promptly and not reworn until the soluble chromic or chromous salts are removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of liquids or solids containing soluble chromic or chromous salts contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquids or solids containing soluble chromic or chromous salts, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with soluble chromic or chromous salts should be promptly washed or showered to remove any soluble chromic or chromous salts.

• Employees who handle liquids or solids containing soluble chromic or chromous salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble chromic or chromous salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in textile treatment in dyeing, printing, moth-proofing, and water-proofing; use in tanning of leather in gloves, garments, and shoe uppers	Local exhaust ventilation; personal protective equipment
Use in manufacture of pigments for green varnishes, inks, paints, and glazes	Local exhaust ventilation; personal protective equipment
Use for metal treatment and polishing	Local exhaust ventilation; personal protective equipment
Use in photographic fixing baths for hardening of emulsions; use as catalysts and in manufacture of catalysts	Local exhaust ventilation; personal protective equipment
Use in chemical synthesis; use as corrosion inhibitors	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquids or solids containing soluble chromic or chromous salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

• **Skin Exposure**

If liquids or solids containing soluble chromic or chromous salts get on the skin, promptly flush the contaminated skin with water. If liquids or solids containing soluble chromic or chromous salts penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of soluble chromic or chromous salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When liquids or solids containing soluble chromic or chromous salts have been swallowed give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If soluble chromic or chromous salts are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing soluble chromic or chromous salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Soluble chromic or chromous salts may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

RESPIRATORY PROTECTION FOR SOLUBLE CHROMIC AND CHROMOUS SALTS (AS CHROMIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate Concentration	
2.5 mg/m³ or less	Any dust and mist respirator, except single-use.**
5 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.** Any fume respirator or high efficiency particulate respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 250 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Chromium Metal and Insoluble Chromium Salts*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all chromium metal and insoluble chromium salts. Physical and chemical properties of some specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Metallic chromium

- Formula: Cr
- Synonyms: None
- Appearance and odor: Shiny, odorless metal.

Copper chromite

- Formula: $Cu_2Cr_2O_4$
- Synonyms: Cuprous chromite
- Appearance and odor: Greenish-blue, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chromium metal or insoluble chromium salts is 1 milligram of chromium metal or insoluble chromium salts per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: The non-carcinogenic forms are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to 0.001 Cr (VI) mg/m^3 and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to 0.025 Cr (VI) mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.05 Cr (VI) mg/m^3 averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chromium metal or insoluble chromium salts can affect the body if they are inhaled. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Ferro chrome alloys have been associated with lung changes in workers exposed to these alloys. Chromite dust exposure may cause minor lung changes.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chromium metal or insoluble chromium salts.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chromium metal or insoluble chromium salts at potentially hazardous levels:

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Chromium and its insoluble salts may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Insoluble chromium salts are reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

The dusts of chromium metal and its insoluble salts, chiefly the chromites, are usually reported to be relatively nontoxic; this is debatable, since exposures associated with toxic effects are usually mixed exposures involving several hexavalent chromium compounds. Ferrochrome alloys have been associated with pulmonary disease in humans. Four workers engaged in the production of ferrochrome alloys developed a nodular type of pulmonary disease with impairment of pulmonary function; air concentrations of chromium in this study averaged 0.26 mg/m^3, although other fumes and dusts were also present. This pulmonary problem may be one of hypersensitivity and thus reversible. Other reports state that chest roentgenograms have revealed only "exaggerated pulmonic markings" in workers exposed to chromite dust. The lungs of groups of workers exposed to chromite dust have been shown to be the seat of pneumoconiotic changes consisting of slight thickening of interstitial tissue and interalveolar septa, with histologic fibrosis and hyalinization. Chromite ore roast mixed with sheep fat implanted intrapleurally in rats produced squamous cell carcinomata coexisting with sarcomata of the lungs; the same material implanted in the thighs of rats produced fibrosarcomata. A refractory plant using chromite ore to make chromite brick had no excess of lung cancer deaths over a 14-year period, and it was concluded that chromite alone probably is not carcinogenic.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Metallic chromium**

1. Molecular weight: 52
2. Boiling point (760 mm Hg): 2640 C (4784 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of metallic chromium): Not applicable
5. Melting point: 1900 C (3452 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Copper chromite**

1. Molecular weight: 295.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 5.24
4. Vapor density (air = 1 at boiling point of copper chromite): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Basic potassium zinc chromate**

1. Molecular weight: 873.8
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 3.47
4. Vapor density (air = 1 at boiling point of basic potassium zinc chromate): Not applicable
5. Melting point: Loses water slowly above 100 C (212 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Chromium metal in contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None listed.
4. Special precautions: None listed.

• **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature (metal): 400 C (752 F) (layer); 580 C (1076 F) (cloud)
3. Minimum explosive dust concentration (metal): 230 grams/m^3
4. Extinguishant: Dry sand, dry dolomite, dry graphite

• **Warning properties**

Chromium metal and insoluble salts are not known to be eye irritants.

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

airborne concentrations of chromium metal or insoluble chromium salts. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of chromium metal or insoluble chromium salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for chromium metal and insoluble chromium salts is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solids or liquids containing insoluble chromium salts.

• Clothing contaminated with insoluble chromium salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of insoluble chromium salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the insoluble chromium salts, the person performing the operation should be informed of insoluble chromium salts's hazardous properties.

• Non-impervious clothing which becomes contaminated with insoluble chromium salts should be removed promptly and not reworn until the insoluble chromium salts are removed from the clothing.

• Employees should be provided with and required to use dust- and splashproof safety goggles where solids or liquids containing insoluble chromium salts may contact the eyes.

SANITATION

• Skin that becomes contaminated with insoluble chromium salts should be promptly washed or showered with soap or mild detergent and water to remove any insoluble chromium salts.

• Eating and smoking should not be permitted in areas where solids or liquids containing insoluble chromium salts are handled, processed, or stored.

• Employees who handle solids or liquids containing insoluble chromium salts should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chromium metal or insoluble chromium salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in fabrication of alloys	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in preparation of alloy steels to enhance corrosion- and heat-resistance	Local exhaust ventilation; general dilution ventilation
Use in fabrication of plated products for decoration or increased wear-resistance	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in production of non-ferrous alloys to impart special qualities to the alloys	Local exhaust ventilation; general dilution ventilation
Use in production and processing of insoluble salts	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use as chemical intermediates; use in textile industry in dyeing, silk treating, printing, and moth-proofing wool	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in leather industry in tanning; use in photograhic fixing baths	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as catalysts for halogenation, alkylation, and catalytic cracking of hydrocarbons	Local exhaust ventilation; general dilution ventilation
Use as fuel additives and propellant additives; in photogaphic fixing baths and in ceramics	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If chromium metal or solids or liquids containing insoluble chromium salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

• **Skin Exposure**

If solids or liquids containing insoluble chromium salts get on the skin, wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing insoluble chromium salts penetrate through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of chromium metal or insoluble chromium salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When solids or liquids containing insoluble chromium salts have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If chromium metal or insoluble chromium salts are spilled, the following steps should be taken:

1. Remove all ignition sources where metallic chromium has been spilled.
2. Ventilate area of spill.
3. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing chromium metal or insoluble chromium salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Chromium metal or insoluble chromium salts may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Chromium (as Cr)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

• **Method**

Sampling and analyses may be performed by collection of chromium metal or insoluble chromium salts on a filter, followed by treatment with acid and atomic

RESPIRATORY PROTECTION FOR CHROMIUM METAL AND INSOLUBLE CHROMIUM SALTS (AS CHROMIUM)

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any dust and mist respirator.
10 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CLOPIDOL

INTRODUCTION

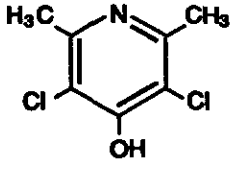
This guideline summarizes pertinent information about clopidol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_7H_7Cl_2NO$

- **Structure**



- **Synonyms**

  3,5-Dichloro-2,6-dimethyl-4-pyridinol; methylchloropindol; clopindol; Farmcoccid; Coccidiostat C; Coyden; Lerbek

- **Identifiers**

  1. CAS No.: 2971-90-6
  2. RTECS No.: UU7711500
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Clopidol is a white to light brown crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 192.06
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: Greater than 320°C (608°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat. In cloud form, clopidol dust may explode if ignited.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of nitrogen) may be released in a fire involving clopidol.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to clopidol; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving clopidol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving clopidol.

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for clopidol is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hr time-weighted average (TWA) concentrations [29 CFR 1910.1000, Table Z-1].

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek and 20 mg/m^3 as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure which should not be exceeded at any time during the workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned clopidol a threshold limit value (TLV) of 10 mg/m^3 (total dust) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The OSHA and ACGIH limits are based on the risk of physical irritation associated with exposure to clopidol.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to clopidol can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Clopidol is an antibiotic used in veterinary medicine as a coccidiostat in poultry. This substance has a low order of acute and chronic toxicity in experimental animals [ACGIH 1991]. The oral LD_{50} in rabbits and guinea pigs is greater than 8 g/kg [NIOSH 1993]. The oral LD_{50} in rats is 18 g/kg [NIOSH 1993; Merck 1983]. Rats fed 15 mg/kg clopidol daily for 2 years showed no adverse effects [ACGIH 1991]. Dogs fed 5 mg/kg clopidol daily (duration of experiment not specified) also showed no adverse effects [ACGIH 1991].

2. *Effects on Humans:* In humans, exposure to clopidol dust may cause physical irritation of the eyes, nose, throat, and skin [NJDH 1986]. No chronic effects have been reported [NJDH 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to clopidol may cause redness and itching of the eyes, runny nose, sore throat, coughing, and redness and irritation of the skin.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to clopidol have been reported.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately***. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of clopidol is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a fluid such as water.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve clopidol and may result in worker exposures to this substance:

—Manufacture and formulation of this substance

—Use as a coccidiostat in poultry

The following methods are effective in controlling worker exposures to clopidol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to toxic substances should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of

adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to clopidol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to clopidol at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to clopidol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of clopidol on the eyes and skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for clopidol.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne clopidol is determined by using a glass fiber filter (37 mm). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected (total dust) or with a 10-mm nylon cyclone preceding the glass fiber filter at a flow rate of 1.7 liter/min until a recommended air volume of 204 liters is collected (respirable fraction). Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If clopidol collects on the skin in excessive amounts, workers should wash the affected areas with soap and water.

Clothing excessively contaminated with clopidol should be removed to avoid local irritation of the skin.

A worker who handles clopidol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or

apply cosmetics in areas where clopidol or a solution containing clopidol is handled, processed, or stored.

STORAGE

Clopidol should be stored in a cool, dry, well-ventilated area in tightly sealed containers. Containers of clopidol should be protected from physical damage and should be stored separately from heat, sparks, and open flame.

SPILLS

In the event of a spill involving clopidol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or disposal.
4. Absorb liquid clopidol-containing formulations in vermiculite, dry sand, earth, or similar material.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Clopidol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of clopidol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of clopidol emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although clopidol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of clopidol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use

only those respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent excessive skin contact with clopidol. Safety glasses, goggles, or face shields should be worn during operations in which clopidol might contact the eyes.

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Occupational Health Guideline for Coal Tar Pitch Volatiles

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

Anthracene

- Formula: $C_{14}H_{10}$
- Synonyms: None
- Appearance and odor: Pale green solid with a faint aromatic odor.

Phenanthrene

- Formula: $C_{14}H_{10}$
- Synonyms: None
- Appearance and odor: Colorless solid with a faint aromatic odor.

Pyrene

- Formula: $C_{16}H_{10}$
- Synonyms: None
- Appearance: Bright yellow solid

Carbazole

- Formula: $C_{12}H_9N$
- Synonyms: None
- Appearance and odor: Colorless solid with a faint aromatic odor.

Benzo(a)pyrene

- Formula: $C_{20}H_{12}$
- Synonyms: BaP, 3,4-benzopyrene
- Appearance and odor: Colorless solid with a faint aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for coal tar pitch volatiles is 0.2 milligram of coal tar pitch volatiles per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for coal tar products be reduced to 0.1 mg/m^3 (cyclohexane-extractable fraction) averaged over a work shift of up to 10 hours per day, 40 hours per week, and that coal tar products be regulated as occupational carcinogens. The NIOSH Criteria Document for Coal Tar Products and NIOSH Criteria Document for Coke Oven Emissions should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Coal tar pitch volatiles can affect the body if they are inhaled or if they come in contact with the eyes or skin.

- **Effects of overexposure**

Repeated exposure to coal tar pitch volatiles has been associated with an increased risk of developing bronchitis and cancer of the lungs, skin, bladder, and kidneys. Pregnant women may be especially susceptible to exposure effects associated with coal tar pitch volatiles. Repeated exposure to these materials may also cause sunlight to have a more severe effect on a person's skin. In addition, this type of exposure may cause an allergic skin rash.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to coal tar pitch volatiles.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to coal tar pitch volatiles at potentially hazardous levels:

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the oral cavity, respiratory tract, bladder, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders, for premalignant and malignant lesions, and evidence of hyperpigmentation or photosensitivity.

—Urinalysis: Coal tar pitch volatiles are associated with an excess of kidney and bladder cancer. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment, as well as a test for red blood cells.

—Urinary cytology: Coal tar pitch volatiles are associated with an excess of kidney and bladder cancer. Employees having 5 or more years of exposure or who are 45 years of age or older should have a urinary cytology examination.

—Sputum cytology: Coal tar pitch volatiles are associated with an excess of lung cancer. Employees having 10 or more years of exposure or who are 45 years of age or older should have a sputum cytology examination.

—14" x 17" chest roentgenogram: Coal tar pitch volatiles are associated with an excess of lung cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Coal tar pitch volatiles are reported to cause an excess of bronchitis. Periodic surveillance is indicated.

—A complete blood count: Due to the possibility of benzene exposure associated with coal tar pitch volatiles, a complete blood count is considered necessary to search for leukemia and aplastic anemia.

—Skin disease: Coal tar pitch volatiles are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, and semi-annually for employees 45 years of age or older or with 10 or more years' exposure to coal tar pitch volatiles.

- **Summary of toxicology**

Coal tar pitch volatiles (CTPV) are products of the destructive distillation of bituminous coal and contain polynuclear aromatic hydrocarbons (PNA's). These hydrocarbons sublime readily, thereby increasing the amounts of carcinogenic compounds in working areas. Epidemiologic evidence suggests that workers intimately exposed to the products of combustion or distillation of bituminous coal are at increased risk of cancer at many sites. These include cancer of the respiratory tract, kidney, bladder, and skin. In a study of coke oven workers, the level of exposure to CTPV and the length of time exposed were related to the development of cancer. Coke oven workers with the highest risk of cancer were those employed exclusively at topside jobs for 5 or more years, for whom the increased risk of dying from lung cancer was 10-fold; all coke oven workers had a 7-½-fold increase in risk of dying from kidney cancer. Although the causative agent or agents of the cancer in coke oven workers is unidentified, it is suspected that several PNA's in the CTPV generated during the coking process are involved. Certain industrial populations exposed to coal tar products have a demonstrated risk of skin cancer. Substances containing PNA's which may produce skin cancer also produce contact dermatitis; examples are coal tar, pitch, and cutting oils. Although allergic dermatitis is readily induced by PNA's in guinea pigs, it is only rarely reported in humans from occupational contact with PNA's; these have resulted largely from the therapeutic use of coal tar preparations. Components of pitch and coal tar produce cutaneous photosensitization; skin eruptions are usually limited to areas exposed to the sun or ultraviolet light. Most of the phototoxic agents will induce hypermelanosis of the skin; if chronic photodermatitis is severe and prolonged, leukoderma may occur. Some oils containing PNA's have been associated with changes of follicular and sebaceous glands which commonly take the form of acne. There is evidence that exposures to emissions at coke ovens and gas retorts may be associated with an increased occurrence of chronic bronchitis. Coal tar pitch volatiles may be associated with benzene, an agent suspected of causing leukemia and known to cause aplastic anemia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Anthracene**
  1. Molecular weight: 178.2
  2. Boiling point (760 mm Hg): 340 C (644 F)
  3. Specific gravity (water = 1): 1.24
  4. Vapor density (air = 1 at boiling point of anthracene): 6.15
  5. Melting point: 217 C (423 F)
  6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Physical data—Phenanthrene**
  1. Molecular weight: 178.2
  2. Boiling point (760 mm Hg): 340 C (644 F)
  3. Specific gravity (water = 1): 1.18
  4. Vapor density (air = 1 at boiling point of phenanthrene): 6.15
  5. Melting point: 100.5 C (213 F)
  6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Physical data—Pyrene**
  1. Molecular weight: 202.3
  2. Boiling point (760 mm Hg): Greater than 360 C (greater than 680 F)

3. Specific gravity (water = 1): 1.28
4. Vapor density (air = 1 at boiling point of pyrene): 6.9
5. Melting point: 150.4 C (303 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Carbazole**

1. Molecular weight: 167.2
2. Boiling point (760 mm Hg): 355 C (671 F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of carbazole): 5.8
5. Melting point: 246 C (475 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Benzo(a)pyrene**

1. Molecular weight: 252.3
2. Boiling point (760 mm Hg): Greater than 360 C (greater than 680 F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of benzo(a)pyrene): 8.7
5. Melting point: 179 C (354 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

• **Flammability**

1. Flash point: Anthracene: 121 C (250 F) (closed cup); Others: Data not available
2. Autoignition temperature: Anthracene: 540 C (1004 F); Others: Data not available
3. Flammable limits in air, % by volume: Anthracene: Lower: 0.6; Others: Data not available
4. Extinguishant: Foam, dry chemical, and carbon dioxide

• **Warning properties**

Grant states that "coal tar and its various crude fractions appear principally to cause reddening and squamous eczema of the lid margins, with only small erosions of the corneal epithelium and superficial changes in the stroma, which disappear in a month following exposure. Chronic exposure of workmen to tar fumes and dust has been reported to cause conjunctivitis and discoloration of the cornea in the palpebral fissure, either near the limbus or, in extreme cases, across the whole cornea. Occasionally, epithelioma of the lid margin has been attributed to contact with coal tar."

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Coal tar products may be sampled by collection on a glass fiber filter with subsequent ultrasonic extraction and weighing. An analytical method for coal tar pitch volatiles is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with condensed coal tar pitch volatiles, where skin contact may occur.

• If employees' clothing may have become contaminated with coal tar pitch volatiles, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with coal tar pitch volatiles

should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of coal tar pitch volatiles from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the coal tar pitch volatiles, the person performing the operation should be informed of coal tar pitch volatiles's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where condensed coal tar pitch volatiles may contact the eyes.

SANITATION

• Workers subject to skin contact with coal tar pitch volatiles should wash with soap or mild detergent and water any areas of the body which may have contacted coal tar pitch volatiles at the end of each work day.

• Employees who handle coal tar pitch volatiles should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

• Areas in which exposure to coal tar pitch volatiles may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to coal tar pitch volatiles may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from extraction and packaging from coal tar fraction of coking	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a binding agent in manufacture of coal briquettes used for fuel; use as a dielectric in the manufacture of battery electrodes, electric-arc furnace electrodes, and electrodes for alumina reduction	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of roofing felts and papers and roofing	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use for protective coatings for pipes for underground conduits and drainage; use as a coating on concrete as waterproofing and corrosion-resistant material; use in road paving and sealing	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture and repair of refractory brick; use in production of foundry cores; use in manufacture of carbon ceramic items	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If condensed coal tar pitch volatiles get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

• **Skin Exposure**

If condensed coal tar pitch volatiles get on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands before eating or smoking and to wash thoroughly at the close of work.

• **Breathing**

If a person breathes in large amounts of coal tar pitch volatiles, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.

• If coal tar pitch volatiles are released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of spill.

2. Collect released material in the most convenient and safe manner for reclamation or for disposal in sealed containers in a secured sanitary landfill.

• Waste disposal method:

Coal tar pitch volatiles may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR COAL TAR PITCH VOLATILES

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m³
Particulate and Vapor Concentration	
2 mg/m³ or less	A chemical cartridge respirator with an organic vapor cartridge(s) and with a fume or high-efficiency filter. Any supplied-air respirator. Any self-contained breathing apparatus.
10 mg/m³ or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s) and with a fume or high-efficiency filter. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and with a full facepiece and a fume or high-efficiency filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode. A powered air-purifying respirator with an organic vapor cartridge and a high-efficiency particulate filter.
400 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 400 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Cobalt Metal Fume and Dust

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formulas of example compounds: Co/CoO/Co_2O_3/Co_3O_4
- Synonyms: None
- Appearance and odor: Odorless black solid or finely divided particulate dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cobalt metal fume and dust is 0.1 milligram of cobalt metal fume and dust per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for cobalt metal fume and dust a Threshold Limit Value of 0.05 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cobalt metal fume and dust can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

Cobalt metal fume and dust cause irritation of the nose and throat. They have also been reported to cause respiratory disease with symptoms ranging from cough and shortness of breath to permanent disability and death. The symptoms frequently go away when exposure is stopped, but sometimes the symptoms progress after exposure has ceased. Exposure to cobalt may cause an allergic skin rash.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cobalt metal fume and dust.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cobalt metal fume and dust at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Cobalt may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Cobalt is reported to decrease pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Cobalt metal fume and dust cause upper respiratory tract irritation, chronic interstitial pneumonitis, and skin sensitization. Rhabdomyosarcomata developed in rats injected intramuscularly with the powder of either pure cobalt metal or cobalt oxide. Animals were exposed to the repeated inhalation of the cobalt metal blend used by the cemented carbide industry: a concentration of 20 mg/m^3 of cobalt for 3 years produced hyperplasia of the bronchial epithelium and focal fibrotic lesions of the lungs with developing granulomata; daily inhalation of cobalt metal fume composed of approximately equal parts of cobalt, cobalt oxide, and cobaltic-cobaltous

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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oxide did not elicit these reactions. Guinea pigs developed acute pneumonitis, often rapidly fatal, from the intratracheal injection of cobalt metal or repeated inhalation of a mixture of 75% tungsten carbide and 25% cobalt. Chronic interstitial pneumonitis has been reported in workers in the cemented carbide industry, and cobalt has been conditionally implicated as the etiologic agent by a process of elimination of the other materials used in the industry. Symptoms range from shortness of breath, cough, and dyspnea on exertion to permanent disability or death in some cases. Among 12 workers exposed to cobalt engaged in manufacture of, or grinding with, tungsten carbide tools, who developed interstitial lung disease, there were 8 fatalities; serial chest roentgenograms over a period of 3 to 12 years revealed gradually progressive densities of a linear and nodular nature which gradually involved major portions of both lungs; cough, dyspnea on exertion, and reduced pulmonary function occurred early in the course of the disease. The disease has features of hypersensitivity; only a small percentage of people exposed are affected and with little evidence of dose-response relationship. Cobalt and its compounds produce an allergic dermatitis of an erythematous papular type, which usually occurs in skin areas subjected to friction, such as the ankles, elbow flexures, and sides of the neck.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 58.93 to 181.9
  2. Boiling point (760 mm Hg): 3100 C (5612 F)
  3. Specific gravity (water = 1): 8.8
  4. Vapor density (air = 1 at boiling point of cobalt metal fume and dust): Not applicable
  5. Melting point: 1491 C (2715 F)
  6. Vapor pressure at 20 C (68 F): 0 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact of dust with strong oxidizers may cause fire and explosions.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Flash point: Not applicable
  2. Autoignition temperature: Specially prepared (the form prepared by reducing the oxides in hydrogen) very fine cobalt dust will catch fire at room temperature in air.
  3. Flammable limits in air, % by volume: Not applicable
  4. Extinguishant: Dry sand, dry dolomite, dry graphite powder
- **Warning properties**

The AIHA *Hygienic Guide* states that "cobalt appears to be an eye irritant. One of the findings in the study of the tungsten carbide industry was a significant amount of conjunctivitis, presumably caused by the cobalt used as 'cement'." Contact with industry has indicated that workers in the cobalt-cemented tungsten industry have not experienced eye irritation to cobalt below 1 mg/m^3.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cobalt metal fume and dust on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for cobalt metal fume and dust is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact

with cobalt dust.

• If employees' clothing may have become contaminated with cobalt dust, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with cobalt dust should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cobalt dust from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cobalt dust, the person performing the operation should be informed of cobalt dust's hazardous properties.

• Non-impervious clothing which becomes contaminated with cobalt dust should be removed promptly and not reworn until the cobalt dust is removed from the clothing.

SANITATION

• Skin that becomes contaminated with cobalt dust should be promptly washed or showered with soap or mild detergent and water to remove any cobalt dust.

• Eating and smoking should not be permitted in areas where cobalt metal fume or dust are generated, handled, processed, or stored.

• Employees who handle cobalt metal fume or dust should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cobalt metal fume and dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use as a binder in manufacture of cemented carbide items; during refining and concentration of ores; during preparation of alloys	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of metal items from magnetic alloy; during manufacture of metal items from super- and high-temperature alloys	Local exhaust ventilation; personal protective equipment
Liberation during grinding and sharpening of cemented carbide and steel tools; during synthesis of cobalt compounds for use as pigments and as catalysts and driers; during refining and concentrations of ores	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of metal items from cutting tool and tool steels; during manufacture of metal items from hard-facing alloys; during manufacture of items containing low-expansion alloys; during manufacture of metal items containing constant-modulus alloys; metal to glass seals in electric lamps, vacuum tubes, and x-ray tubes	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of dental prosthetic and osteosynthetic items; during asbestos fiber processing	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If cobalt metal dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

• **Skin Exposure**

If cobalt metal fume or dust get on the skin, wash the contaminated skin using soap or mild detergent and water. If cobalt metal dust penetrates through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of cobalt metal fume or dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respi-

ration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When cobalt metal dust has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or releases until cleanup has been completed.

• If cobalt dust is spilled or if potentially hazardous amounts of cobalt metal fume are inadvertently released, the following steps should be taken:

1. Ventilate area of spill.
2. Collect released material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill.

• Waste disposal method:

Cobalt dust may be placed in sealed containers and disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR COBALT METAL FUME AND DUST

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.
1.0 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COBALT CARBONYL

INTRODUCTION

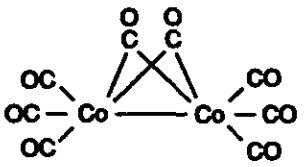
This guideline summarizes pertinent information about cobalt carbonyl (measured as Co) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_8Co_2O_8$

- **Structure**



- **Synonyms**

Cobalt octacarbonyl, cobalt tetracarbonyl, cobalt tetracarbonyl dimer, di-μ-carbonylhexacarbonyl-dicobalt, dicobalt carbonyl, dicobalt octacarbonyl, octacarbonyldicobalt

- **Identifiers**

1. CAS No.: 10210-68-1
2. RTECS No.: GG0300000
3. DOT UN: 9188 31 (Hazardous substance, liquid, or solid, n.o.s.)
4. DOT label: None

- **Appearance and odor**

Cobalt carbonyl is an orange to dark brown crystalline solid, although the pure substance is white.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 341.94
2. Boiling point (at 760 mm Hg): Decomposes at temperatures above 52°C (125.6°F)
3. Specific gravity (water = 1): 1.87 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 51°C (123.8°F)
6. Vapor pressure at 15°C (59°F): 0.07 mm Hg
7. Solubility: Insoluble in water; soluble in alcohol, ether, naphtha, and carbon disulfide
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Exposure of cobalt carbonyl to air or heat causes decomposition to occur. Cobalt carbonyl is slowly attacked by sulfuric

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acid or hydrochloric acid and is more rapidly attacked by bromine and nitric acid.

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) and the pyrophoric dodecacarbonyltetracobalt may be released in a fire involving cobalt carbonyl.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to cobalt carbonyl.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Data not available

4. Extinguishant: For small fires involving cobalt carbonyl, use dry chemical, carbon dioxide, water spray, or standard foam. For large fires, use water spray, fog, or standard foam.

Fires involving cobalt carbonyl should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Containers of cobalt carbonyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Do not scatter this material with high-pressure water streams. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cobalt carbonyl. Structural firefighters' protective clothing may provide limited protection against fires involving this substance.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cobalt carbonyl (measured as Co) [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cobalt carbonyl (measured as Co) a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation. The ACGIH limit is based on the risk of pulmonary and other acute effects associated with exposure to cobalt carbonyl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cobalt carbonyl can occur through inhalation, ingestion, and contact with the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cobalt carbonyl damages the respiratory and central nervous systems, liver, and kidneys, and may also irritate and sensitize the skin of animals on contact. Administered topically or subcutaneously to rats and mice, cobalt carbonyl was absorbed through the skin in toxic amounts and caused irritation of the skin [NLM 1990]. Applied to the skin of guinea pigs, cobalt carbonyl caused an allergic reaction [NLM 1990]. The LC_{50} (duration unspecified) in rats is 165 mg/m^3 [NIOSH 1989] and the 2-hr LC_{50} in mice is 27 mg/m^3 [Sax and Lewis 1989]. Rats exposed to concentrations of cobalt carbonyl ranging from 8 to 44 mg/m^3 for 30 min showed inflammatory and proliferative changes in the lungs at autopsy; at the highest concentrations, there was evidence of pulmonary edema. Histopathological changes and adverse effects on the central nervous system, liver, and kidneys were seen at autopsy; decreased thyroid function was also observed in these animals [NLM 1990]. The oral LD_{50} is 754 mg/kg in

rats [NIOSH 1989] and 378 mg/kg in mice [Sax and Lewis 1989].

2. *Effects on Humans:* Cobalt carbonyl causes sensory irritation on contact with the skin and mucous membranes [Parmeggiani 1983], and affects the respiratory system and the blood. Factory workers acutely overexposed to airborne cobalt carbonyl developed bronchospasm, showed X-ray evidence of focal infiltrations of the lungs, and had changes in several cellular blood components [NLM 1990]. Based on the toxicologic similarities between nickel carbonyl and cobalt carbonyl, it is likely that overexposure to cobalt carbonyl would give rise to nausea, headache, dizziness, coughing, dyspnea, and substernal pain [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cobalt carbonyl may cause cough, shortness of breath, lung densities, decreased pulmonary function, wheezing, and pain in the chest. Clinical evidence of changes in the cellular components of the blood may also be present. Ingestion could cause pericardial effusion, pain, vomiting, nerve deafness, convulsions, and thyroid enlargement.

2. *Chronic exposure:* Continued low-level exposure to cobalt carbonyl may cause cough, rapid breathing on exertion, decreased pulmonary function, wheezing, and shortness of breath.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove all contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cobalt carbonyl or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do not give syrup of ipecac because of possible onset of respiratory depression and seizures.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cobalt carbonyl and result in worker exposures to this substance:

—Use as a catalyst for organic reactions

—Use as a catalyst in the plastics industry

—Preparation of metals of high purity

The following methods are effective in controlling worker exposures to cobalt carbonyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cobalt carbonyl, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory and nervous systems, liver, kidneys, and blood. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cobalt carbonyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory or nervous system, liver, kidneys, or blood.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cobalt carbonyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cobalt carbonyl on the respiratory or nervous system, liver, kidneys, or blood. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cobalt carbonyl.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to cobalt carbonyl may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cobalt carbonyl (measured as cobalt) is determined by using a 0.8 micron mixed cellulose ester filter. Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is included in the OSHA Computerized Information System [OSHA 1990], the *OSHA Analytical Methods Manual* [OSHA 1985], the *OSHA Chemical Information Manual* [OSHA 1987], and in Method 7027 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If cobalt carbonyl contacts the skin, workers should flush the affected areas immediately with plenty of water for at least 15 min, and then wash with soap and water.

Clothing contaminated with cobalt carbonyl should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cobalt carbonyl, particularly its potential to cause headache, nausea, and pulmonary effects.

A worker who handles cobalt carbonyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cobalt carbonyl or a solution containing this substance is handled, processed, or stored.

STORAGE

Cobalt carbonyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of cobalt carbonyl should be protected from physical damage and should be stored separately from hydrochloric acid, sulfuric acid, nitric acid, bromine, heat, sparks, and open flame. Because containers that formerly contained cobalt carbonyl may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving cobalt carbonyl, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Cover the spill area with a plastic sheet or tarp to minimize spreading.

2. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities for hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 10,000 lb or more of cobalt carbonyl must comply with EPA's emergency planning requirements [40 CFR Part 355.30]. (If cobalt carbonyl is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 10 lb or more of cobalt carbonyl are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, dis-

charging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for cobalt carbonyl is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center *immediately* at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cobalt carbonyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cobalt carbonyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cobalt carbonyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with cobalt carbonyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cobalt carbonyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cobalt carbonyl.

If cobalt carbonyl is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cobalt carbonyl might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cobalt carbonyl. Contact lenses should not be worn if the potential exists for cobalt carbonyl exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COBALT HYDROCARBONYL

INTRODUCTION

This guideline summarizes pertinent information about cobalt hydrocarbonyl (measured as cobalt) for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $HCo(CO)_4$

- **Synonyms**

  Tetracarbonylhydrocobalt; hydridotetracarbonyl cobalt; hydrocobalt tetracarbonyl; tetracarbonylhydridocobalt

- **Identifiers**

  1. CAS No.: 16842-03-8
  2. RTECS No.: GG0900000
  3. DOT UN: 1954 22 (Flammable gas, n.o.s.)
  4. DOT label: Flammable gas

- **Appearance and odor**

  Cobalt hydrocarbonyl is a flammable gas that is unstable and decomposes rapidly at room temperature.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 171.98
  2. Boiling point (760 mm Hg): Data not available
  3. Specific gravity: Data not available
  4. Relative gas density: 5.93
  5. Freezing point: -26.2°C (-15.2°F)
  6. Vapor pressure at 20°C (68°F): >1 atm
  7. Solubility: Sparingly soluble in water
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Contact of cobalt hydrocarbonyl with air causes decomposition.
  2. Incompatibilities: None reported
  3. Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving cobalt hydrocarbonyl.
  4. Special precautions: None reported

- **Flammability**

  The National Fire Protection Association has not assigned a flammability rating for cobalt hydrocarbonyl; however, this substance is flammable.

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National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Flash point: Not applicable (Flammable gas)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical or carbon dioxide for small fires and water spray or fog for large fires.

Fires involving cobalt hydrocarbonyl should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cobalt hydrocarbonyl may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions, and let the tank car or truck burn unless the leak can be stopped. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cobalt hydrocarbonyl. Structural firefighters' protective clothing will provide limited protection.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cobalt hydrocarbonyl [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cobalt hydrocarbonyl a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation associated with exposure to cobalt hydrocarbonyl. The ACGIH limit is based on the risk of lung, liver, and kidney effects associated with exposure to cobalt hydrocarbonyl.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cobalt hydrocarbonyl can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cobalt hydrocarbonyl affects the respiratory system. The 2-hr LC_{50} for cobalt hydrocarbonyl is 46.2 mg/m^3 in rats and 17.5 mg/m^3 in mice [NIOSH 1993]. Acutely poisoned animals showed signs of chemical pneumonitis before death [Palmer et al. 1959]. Dogs, rats, and guinea pigs exposed 6-hr/day on 71 occasions within a 3-month period to cobalt hydrocarbonyl decomposition products at an average cobalt concentration of 9 mg/m^3 showed elevated hemoglobin levels (rats) and foam cell aggregates in the lungs; these signs disappeared after the cessation of exposure [Palmer et al. 1959].

2. *Effects on Humans:* No adverse effects of exposure to cobalt hydrocarbonyl have been reported in humans.

- **Signs and symptoms of exposure**

1. *Acute or sub-chronic exposure:* Based on effects seen in animals, subchronic exposure to cobalt hydrocarbonyl may cause difficult breathing, coughing, reduced lung function, and fluid in the lungs.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to cobalt hydrocarbonyl have been reported.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cobalt hydrocarbonyl and may result in worker exposures to this substance:

—Manufacture of cobalt hydrocarbonyl

—Use as a catalyst

The following are methods that are effective in controlling worker exposures to cobalt hydrocarbonyl, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cobalt hydrocarbonyl, the licensed health

care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cobalt hydrocarbonyl at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cobalt hydrocarbonyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cobalt hydrocarbonyl on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cobalt hydrocarbonyl.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cobalt hydrocarbonyl (measured as cobalt) is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a recommended flow rate of 2.0 liters/min until a recommended air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy for total cobalt. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cobalt hydrocarbonyl contacts the skin, the victim should immediately and thoroughly wash the affected areas with soap and water.

Clothing contaminated with cobalt should be removed immediately.

A worker who is exposed to cobalt hydrocarbonyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cobalt hydrocarbonyl is generated.

STORAGE

Cobalt hydrocarbonyl should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of cobalt hydrocarbonyl should be protected from physical damage and should be stored separately from air, heat, sparks, and open flame.

LEAKS

In the event of a leak involving cobalt hydrocarbonyl, persons not wearing protective equipment and clothing

should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a leak:

1. Notify safety personnel.

2. Remove all sources of heat and ignition.

3. Ventilate potentially explosive atmospheres.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cobalt hydrocarbonyl is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cobalt hydrocarbonyl; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cobalt hydrocarbonyl emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cobalt hydrocarbonyl is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cobalt hydrocarbonyl exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowl-

edgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with cobalt hydrocarbonyl. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cobalt hydrocarbonyl permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cobalt hydrocarbonyl.

Safety glasses, goggles, or face shields should be worn during operations in which cobalt hydrocarbonyl might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cobalt hydrocarbonyl.

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Occupational Health Guideline for Copper Dusts and Mists

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formulas of example compounds: $CuSO_4 \cdot 5H_2O$; CuCl
- Example compounds: Copper sulfate dust or mist; cuprous chloride dust
- Appearance and odor: Odorless solids

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for copper dusts or mists is 1 milligram of copper dusts or mists per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Copper dusts or mists can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Powdered copper or dusts or mists of copper salts may cause a feeling of illness similar to the common cold with sensations of chills and stuffiness of the head. Small copper particles may enter the eye and cause irritation, discoloration, and damage.

2. Long-term Exposure: Repeated or prolonged exposure to copper dusts or mists may cause skin irritation or discoloration of the skin or hair.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to copper dusts or mists.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to copper dusts and mists at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from copper dusts and mists exposure.

—Chronic respiratory disease: Copper dusts or mists cause respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of copper dusts or mists might cause exacerbation of symptoms due to their irritant properties.

—Liver disease: Copper dusts or mists cause liver damage in animals. Persons with pre-existing liver disease may be more susceptible to the effects of these agents.

—Kidney disease: Copper dusts or mists cause kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: Skin sensitization in human subjects has occurred. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

—Hematopoietic disorders: Anemia has occurred in animals given copper salts orally. Persons with pre-existing blood disorders may be more susceptible to the effects of these agents.

—Wilson's disease: Persons with pre-existing Wilson's disease may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Inhalation of dusts and mists of copper and copper salts results in irritation of the upper respiratory tract, with occasional ulceration and perforation of the nasal septum. Inhalation of copper and its compounds by animals caused injury to the lungs and liver with

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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hemochromatosis. Access of sheep to salt licks containing 5 to 9% copper sulfate caused the sudden onset of hemolytic anemia, icterus, and hemoglobinuria followed by death in a day or two; at necropsy, the liver, kidneys, and spleen showed severe degenerative changes. Workers exposed to copper dust in concentrations of 0.075 to 0.120 mg/m³ complained of mild nasal discomfort. Exposure to the dust of copper acetate produced sneezing, coughing, digestive disorders, and fever. Metal workers exposed to complex copper salts in dust form complained of metallic taste with irritation of nasal and oral mucosa; atrophic changes in the mucous membranes were noted in subjects exposed for long periods of time. On ingestion, copper salts act as irritants and cause nausea, vomiting, abdominal pain, hemorrhagic gastritis, and diarrhea. Copper salts splashed in the eye cause conjunctivitis, corneal ulceration, and turbidity, and may produce palpebral edema. Copper particles embedded in the eye result in pronounced foreign-body reaction with characteristic discoloration of ocular tissue. Allergic contact dermatitis due to copper exposure, although rare, has been reported. Greenish discoloration of the skin and hair of some copper workers has been observed. Although copper is an essential element for health, excessive amounts can produce harmful effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: $CuSO_4$: 249.7; $CuCl_2$: 99
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of copper dusts or mists): Not applicable
5. Melting point: Higher than 100 C (212 F). For example, copper sulfate = 150 C (302 F); cuprous chloride = 430 C (806 F)
6. Vapor pressure at 20 C (68 F): Not applicable
7. Solubility in water, g/100 g water at 20 C (68 F): Ranges from very low (e.g. cuprous chloride = 0.006) to high (e.g. copper sulfate = 35)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Extreme heat
2. Incompatibilities: Copper dusts or mists may react with acetylene gas to form copper acetylides, which are solids that are sensitive to shock. Some copper mists may react with magnesium metal to form flammable hydrogen gas.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Ignition temperature: Copper dusts = 700 C (1292 F)

- **Warning properties**

According to Grant, copper acetoarsenite, copper chloride, copper sulfate, copper carbonate and oxide, and copper metal all produce local irritant effects when in contact with the eye. The *Documentation of TLV's* also notes that copper salts on the eye may cause "conjunctivitis or even ulceration and turbidity of the cornea." Concentrations producing these effects are not given.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of copper dusts or mists on a cellulose ester membrane filter, followed by treatment with nitric acid, solution in hydrochloric acid, and atomic absorption spectrophotometric analysis. An analytical method for copper dusts or mists is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with copper salts or liquids containing copper salts.

- If employees' clothing may have become contaminated with powdered copper, copper salts, or liquids containing copper salts, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with copper salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of copper salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the copper salts, the person performing the operation should be informed of copper salts's hazardous properties.
- Non-impervious clothing which becomes contaminated with copper salts should be removed promptly and not reworn until the copper salts are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where powdered copper or dusts, mists, or liquids containing copper salts may contact the eyes.

SANITATION

- Skin that becomes contaminated with copper salts should be promptly washed or showered with soap or mild detergent and water to remove any copper salts.
- Eating and smoking should not be permitted in areas where powdered copper, copper salts, or liquids containing copper salts are handled, processed, or stored.
- Employees who handle powdered copper, copper salts, or liquids containing copper salts should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to copper dusts or mists may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining, extracting, and refining copper ore; during fabrication and manufacture of copper rod, wire, piping, and tubing for use in electrical, plumbing, and building industries; during manufacture of domestic utensils; during manufacture of alloys	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from production and application of fungicides, insecticides, and germicides for soil, feed, grain, textile, water and sewage treatments; during use of copper salts for paint pigments and coloring agents, electroplating baths, wood preservation, automotive emission controls, textile treatment, and organic synthesis	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If copper dusts or mists get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If copper salts or liquids containing copper salts get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If copper salts or liquids containing copper salts penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of copper dusts or mists, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When powdered copper, copper salts, or liquids containing copper salts have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of release until cleanup has been completed.

• If copper dusts or mists are spilled or released, the following steps should be taken:

1. Ventilate area of release.
2. Collect spilled material in the most convenient and safe manner for reclamation, or for disposal in a secured sanitary landfill. Liquid containing copper should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Copper dusts or mists and copper compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR COPPER DUSTS AND MISTS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Copper Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Cu/Cu_2O/CuO
- Synonyms: None
- Appearance: Finely divided particulate dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for copper fume is 0.1 milligram of copper fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for copper fume a Threshold Limit Value of 0.2 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Copper fume can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Copper fume causes irritation of the eyes, nose, and throat, and a flu-like illness called metal fume fever. Symptoms of metal fume fever include fever, muscle aches, nausea, chills, dry throat, cough, and weakness. It may also cause a metallic or sweet taste in the mouth.

2. Long-term Exposure: Repeated or prolonged exposure to copper fume may cause the skin and hair to change color.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to copper fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to copper fume at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from copper fume exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of copper fume might cause exacerbation of symptoms due to its irritant properties.

—Hepatolenticular degeneration (Wilson's disease): Persons with pre-existing Wilson's disease may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Inhalation of copper fume results in irritation of the upper respiratory tract and an influenza-like illness termed metal fume fever. Signs and symptoms of metal fume fever include chills, muscle aches, nausea, fever, dry throat, cough, weakness, and lassitude. There is usually leucocytosis, which may amount to 12,000 to 16,000/ml; recovery is usually rapid, and there are no sequelae. Most workers develop an immunity to these attacks, but it is quickly lost; attacks tend to be more severe on the first day of the work-week. Other effects from copper fume are irritation of the upper respiratory tract, metallic or sweet taste, and in some instances discoloration of the skin and hair. Exposure of workers to concentrations of 1 to 3 mg/m^3 for short periods resulted in altered taste response but no nausea; levels of from 0.02 to 0.4 mg/m^3 produced no complaints. Transient irritation of the eyes has followed exposure to a

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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fine dust of oxidation products of copper produced in an electric arc.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 63.5 to 143.1
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): Not applicable
  4. Vapor density (air = 1 at boiling point of copper fume): Not applicable
  5. Melting point: Not applicable
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with acetylene gas may cause formation of copper acetylides that are sensitive to shock.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not applicable
- **Warning properties**

Copper fume is not known to be a significant eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of copper fume on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for copper fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to copper fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during construction and installation of materials fabricated from copper metal or copper alloys; during copper metal processing of castings, sheets, rods, tubing, and wire; during copper metal smelting and refining operations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of copper fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of copper fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Copper as Cu," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR COPPER FUME

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
1 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR COTTON DUST

INTRODUCTION

This guideline summarizes pertinent information about cotton dust for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

"Cotton dust" is defined as dust generated into the atmosphere as a result of the processing of cotton fibers combined with any naturally occurring materials such as stems, leaves, bracts, and inorganic matter which may have accumulated on the cotton fibers during the growing or harvesting period. Any dust generated from the processing of cotton through the weaving of fabric in textile mills and dust generated in other operations or manufacturing processes using new or waste cotton fibers or cotton fiber by-products from textile mills is also considered cotton dust.

SUBSTANCE IDENTIFICATION

• **Identifiers:** RTECS GN2275000; DOT 1365 (cotton, wet or contaminated), label required: "Spontaneously Combustible"

• **Appearance:** Whitish solid (fibers and/or particulates)

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Specific gravity (water = 1): 1.3 (approximate)
2. Insoluble in water

• **Reactivity**

Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

• **Flammability**

1. Minimum ignition temperature: 470°C (878°F), cotton flock
2. Minimum explosive dust concentration: 0.05 g/L (50 g/m³), cotton flock
3. Extinguishant: Water
4. Combustible solid (NFPA)

• **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, cotton dust should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cotton dust is 200 micrograms of cotton dust per cubic meter of air ($\mu g/m^3$) as a time-weighted average (TWA) concentration over an 8-hour workshift in yarn manufacturing and cotton washing operations; 750 $\mu g/m^3$ as a TWA over an 8-hour workshift in textile slashing and weaving operations; and 500 $\mu g/m^3$ as a TWA over an 8-hour workshift in textile mill waste house operations and dust from lower grade washed cotton in yarn manuacturing; and 1,000 $\mu g/m^3$ as a TWA over an 8-hour workshift in cotton waste processing operations of waste recycling (sorting, blending, cleaning, willowing, and garnetting). The National Institute for Occupational Safety and Health (NIOSH) recommends that exposure to cotton dust be reduced to the lowest feasible limit, which is defined as being a recommended exposure limit (REL) of less than 200 $\mu g/m^3$. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for cotton dust (raw) is 200 $\mu g/m^3$ as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cotton dust

	Exposure limits $\mu g/m^3$
OSHA PEL TWA	200 (yarn manufacturing and cotton washing)
	750 (slashing and weaving)
	500 (textile mill waste house operations and lower grade washed cotton in yarn manufacturing)
	1,000 (waste recycling and garnetting)
NIOSH REL	<200
ACGIH TLV TWA	200

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Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• Routes of exposure

Cotton dust may cause adverse health effects following exposure via inhalation.

• Summary of toxicology

1. *Effects on animals:* In rabbits, inhalation of cotton dust combined with bacterial *(Escherichia coli)* endotoxin caused bronchitis.

2. *Effects on humans:* Short-term exposure to cotton dust has caused bronchitis and acute byssinosis (also known as "Brown Lung" or "Monday Morning Fever"), a reversible respiratory disease produced by inhalation of cotton dust. Chronic exposure has caused lung airway obstruction (which reduces ventilatory capacity) and has led to disability and premature death. A direct relationship has been observed between the total concentration of cotton dust exposure and the rate of development of byssinosis. Among workers exposed to cotton dust, cigarette smokers have an increased risk of developing byssinosis. The biologically active material in cotton dust has not been ascertained; however, the risk of developing byssinosis appears to be reduced for workers who are exposed to dust from washed cotton.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to cotton dust can produce a feeling of chest tightness, coughing, wheezing, phlegm, weakness, fever, chills, and breathing difficulty (dyspnea). These symptoms can disappear following removal from exposure (during brief periods away from work) and can reappear following reexposure.

2. *Long-term (chronic):* Exposure to cotton dust can cause permanent and disabling breathing difficulties that include chronic bronchitis with emphysema.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to cotton dust should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to cotton dust, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory tract. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cotton dust at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of asthma or significant breathing impairment due to chronic lung disease. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to cotton dust. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory tract as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, pre- and post-shift tests of lung function, and chest X-rays.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to cotton dust may cause

diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include: Byssinosis (acute form)
2. Delayed-onset SHE's include: Byssinosis (chronic form) and chronic bronchitis with emphysema

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting cotton dust using a vertical elutriator preselector with a high-efficiency membrane filter and analyzing by gravimetric methods. Detailed sampling and analytical methods for cotton dust may be found in the *Criteria for a Recommended Standard. . . .Occupational Exposure to Cotton Dust.*

SANITATION

Cleaning of equipment by "blowing-down" with compressed air or dry sweeping should be avoided. Vacuum cleaning should be instituted for all processes whenever possible. If "blow-down" is necessary, it should be conducted only in the absence of personnel not directly involved in the "blow-down" operation. Those workers involved in "blow-down" should wear adequate respiratory protection.

Good housekeeping practices designed to prevent the resuspension of settled dust shall be developed and followed at all times.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, and the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cotton dust should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cotton dust may occur and control methods which may be effective in each case are listed in Table 2.

EMERGENCY FIRST AID PROCEDURES

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cotton dust, an eye-wash fountain should be provided within the immediate work area for emergency use. Contact lenses should not be worn when working with this substance.

Table 2.—Operations and methods of control for cotton dust

Operations	Controls
During carding operations, mixing and blowing opertions, bale breaking, manufacturing of cotton yarn, and handling of cottonseed in the extraction of cottonseed oil	Process enclosure, local exhaust ventilation, personal protective equipment
During cotton batting operations and weaving of textiles containing cotton yarn	General dilution ventilation
During raw cotton ginning, bale pressing, and harvesting	Local exhaust ventilation, personal protective equipment

SPILLS AND LEAKS

In cases in which environmental levels exceed the NIOSH REL, workers not wearing respiratory protection should be restricted from areas of cotton dust contamination until cleanup has been completed.

If cotton dust contamination occurs, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of contamination.
3. Cotton dust may be collected by vacuuming with an appropriate high-efficiency filtration system or by using wet methods and placed in an appropriate container. If a vacuum system is used, there should be no sources of ignition in the vicinity of the contamination, and sufficient flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cotton dust

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 $\mu g/m^3$	Any dust respirator
Less than or equal to 2,000 $\mu g/m^3$	Any dust respirator except single-use and quarter-mask respirators
	Any supplied-air respirator
	Any air-purifying respirator with a high-efficiency particulate filter
	Any self-contained breathing apparatus
Less than or equal to 5,000 $\mu g/m^3$	Any powered air-purifying respirator with a dust filter
	Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 10,000 $\mu g/m^3$	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
	Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Planned or emergency entry into environments containing unknown concentrations or levels above 10,000 $\mu g/m^3$	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

*Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of <200 $\mu g/m^3$.

Occupational Health Guideline for Crag Herbicide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $2,4\text{-}Cl_2C_6H_3OC_2H_{4G1}{}^{OSO}{}_3Na$
- Synonyms: Sesone; Crag herbicide No. 1; sodium 2-(2,4-dichlorophenoxy)ethyl sulfate
- Appearance and odor: Colorless solid with no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Crag herbicide is 15 milligrams of Crag herbicide per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for Crag herbicide a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Crag herbicide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Animal experiments have shown that exposure to Crag herbicide may cause tremors, muscle spasms, and convulsions. It has also caused congestion of the lungs, liver, and kidneys in animals. A solution of Crag herbicide dropped in animal eyes caused damage. The solution applied to animal skin has caused skin irritation and damage.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Crag herbicide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Crag herbicide at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from Crag herbicide exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Crag herbicide might cause exacerbation of symptoms since it causes pulmonary hemorrhage in animals at lethal doses.

—Liver disease: Crag herbicide causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Crag herbicide causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: Crag herbicide is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Convulsive disorders: Crag herbicide (Sesone) causes convulsions in animals. Persons with a history of such disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Crag herbicide (Sesone) dust affects the nervous system in animals and causes convulsions. In rats the oral LD50 ranged from 0.73 to 1.09 g/kg; effects were a fine

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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muscular tremor, myotonus, a tendency to extend the hind feet caudally, and convulsions. Autopsy findings in animals that died were pulmonary hemorrhage, with mild liver and kidney damage. A 5% aqueous solution dropped in the eye of a rabbit caused corneal necrosis. The application of 0.01 ml of a 5% suspension of Sesone in acetone to the shaved rabbit belly resulted in edema and necrosis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 309
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): Greater than 1
  4. Vapor density (air = 1 at boiling point of Crag herbicide): Not applicable
  5. Melting point: 170 C (338 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 25
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None.
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, sulfur dioxide, and carbon monoxide) may be released when Crag herbicide decomposes.
  4. Special precautions: None.
- **Flammability**
  1. Not combustible.
- **Warning properties**

Union Carbide Corporation, in the *Chemical Company Guide* for Crag herbicide, states that "flooding the rabbit eye with a saturated solution of the chemical in propylene glycol caused a reaction similar to moderate inflammation. The dry powder can be expected to have an additional mechanical irritant action."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for Crag herbicide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with Crag herbicide or liquids containing Crag herbicide.
- If employees' clothing may have become contaminated with Crag herbicide or liquids containing Crag herbicide, employees should change into uncontaminated clothing before leaving the work premises.
- Non-impervious clothing which becomes contaminated with Crag herbicide should be removed promptly and not reworn until the Crag herbicide is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where Crag herbicide or liquids containing Crag herbicide may contact the eyes.

SANITATION

- Skin that becomes contaminated with Crag herbicide should be promptly washed or showered to remove any Crag herbicide.
- Employees who handle Crag herbicide or liquids containing Crag herbicide should wash their hands thoroughly before eating, smoking, or using toilet facilities.
- Eating and smoking should not be permitted in areas where solid Crag herbicide is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Crag herbicide may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of weedicides in agricultural operations	Process enclosure; local exhaust ventilation; personal protective equipment
Application of weedicides in agricultural operations	Personal protective equipment
Manufacture of Crag herbicide	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If Crag herbicide or liquids containing Crag herbicide get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If Crag herbicide or liquids containing Crag herbicide get on the skin, promptly wash the contaminated skin with water. If Crag herbicide or liquids containing Crag herbicide penetrate through the clothing, remove the clothing promptly and wash the skin with water. If irritation is present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of Crag herbicide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When Crag herbicide or liquids containing Crag herbicide have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If Crag herbicide is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing Crag herbicide should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Crag herbicide may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR CRAG HERBICIDE

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate Concentration	
75 mg/m³ or less	Any dust and mist respirator, except single-use.
150 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRESOL, ALL ISOMERS

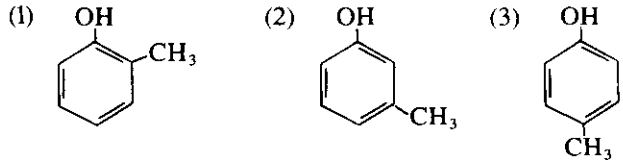
INTRODUCTION

This guideline summarizes pertinent information about the three isomers of cresol (ortho-, meta-, and para-cresol) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines. Throughout this guideline, the term "cresol" refers to any of the three isomers.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Formula:** C_7H_8O
- **Structure:**



- **Synonyms:** (1) o-Cresol; 2-cresol; o-cresylic acid; 1-hydroxy-2-methylbenzene; o-hydroxy toluene;
(2) m-Cresol; 3-cresol; m-cresylic acid; 1-hydroxy-3-methylbenzene; m-hydroxy toluene; 3-hydroxy toluene;
(3) p-Cresol; 4-cresol; p-cresylic acid; 1-hydroxy-4-methylbenzene; p-hydroxy toluene; 4-hydroxy toluene

- **Identifiers:** (1) CAS 95-48-7; RTECS G06300000; DOT 2076; (2) CAS 108-39-4; RTECS G06125000; DOT 2076; (3) CAS 106-44-5; RTECS G06475000; DOT 2076; DOT label required for all isomers: "Poison"

- **Appearance and odor:** Colorless crystals or liquid with an odor like phenol or creosote

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Physical data**

1. Molecular weight: 108.13
2. Boiling point (at 760 mmHg): (1) 191°C (376°F); (2) 202.7°C (397°F); (3) 201.9°C (395°F)
3. Specific gravity (water = 1): (1) 1.048; (2) 1.034; (3) 1.035
4. Vapor density (air = 1 at boiling point of cresol): 3.72
5. Melting point: (1) 30.9°C (87.8°F); (2) 12.0°C (49°F); (3) 34.8°C (95°F)
6. Vapor pressure at 25°C (77°F): (1) 0.25 mmHg; (2) 0.15 mmHg; (3) 0.11 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): (1) 2.5; (2) 2.2; (3) 1.9
8. Evaporation rate (butyl acetate = 1): (1) 0.025; (2) 0.015; (3) 0.011
9. Saturation concentration in air (approximate) at 25°C (77°F): (1) 0.03% (300 ppm); (2) 0.02% (200 ppm); (3) 0.014% (140 ppm)
10. Ionization potential: (1) 8.93 eV; (2) 8.98 eV; (3) 8.97 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents, alkalies, and heat.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and formaldehyde) may be released in a fire involving cresol.
3. Caution: Liquid cresol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: (1) 81.1°C (178°F) (closed cup); (2) 86.1°C (187°F) (closed cup); (3) 86.1°C (187°F) (closed cup)
2. Autoignition temperature: (1) 559°C (1040°F); (2) 626°C (1158°F); (3) 559°C (1040°F)
3. Flammable limits in air, % by volume: (1) Lower, 1.4 at 149°C (300°F); upper, not available; (2) lower, 1.1 at 150°C (302°F); upper, not available; (3) lower, 1.1 at 150°C (302°F); upper, not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

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• **Warning properties**

1. Odor threshold: Less than 1 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, cresol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, cresol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cresol is 5 parts of cresol per million parts of air (ppm) [22 milligrams of cresol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes. The NIOSH REL is 2.3 ppm (10 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (22 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cresol (all isomers)

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	5	22
NIOSH REL TWA	2.3	10
ACGIH TLV® TWA (Skin)	5	22

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Cresol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**

1. *Effects on animals:* In rats and rabbits, acute dermal absorption of cresol caused tremors, convulsions, fluid in the lungs, liver injury, and kidney inflammation; oral administration caused gastrointestinal tract inflammation, pneumonia, injury to the liver and kidneys, convulsions, and coma. Chronic inhalation of cresol by rats and mice produced inflammation and fluid accumulation in the airways, damage to the bone marrow, and degeneration of cells in the brain.
2. *Effects on humans:* Acute exposure to cresol has caused alterations in brain function and death due to respiratory failure. Repeated exposure by any route has produced nervous disorders, fluid in the lungs, and death due to severe damage to the liver, kidneys, pancreas, or spleen.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to cresol can cause muscular weakness, nausea, vomiting, abdominal pain, headache, dizziness, dimness of vision, ringing in the ears, weak pulse, rapid and labored breathing, fainting, and mental confusion and depression. Skin irritation and burns can also occur. Eye contact with cresol can cause extensive damage and blindness.
2. *Long-term (chronic):* Exposure to cresol can cause difficulty in swallowing, vomiting, salivation, loss of appetite, and diarrhea. Skin eruptions, rash, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to cresol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and respiratory and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cresol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include historical and physical or laboratory findings consistent with chronic diseases of the skin or liver. In addition to the medical interview and physical examination, the means to identify these conditions may include serologic screening tests of liver function and markers for hepatitis A or B infection.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to cresol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity or physiologic function of the eyes, skin, liver, kidneys, and respiratory and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. Liver function tests should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at time of job transfer or termination**
The medical, environmental, and occupational history interviews, the physical examination, the selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to cresol may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**
Acute and delayed-onset SHE's include toxic hepatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**
Measurements to determine worker exposure to cresol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**
Sampling and analysis may be performed by collecting cresol with silica gel tubes followed by desorption with acetone and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure cresol may also be used if available. A detailed sampling and analytical method for cresol may be found in the *NIOSH Manual of Analytical Methods* (method number 2001).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with cresol.

Workers should be provided with and required to use dust- and splash-proof safety goggles where cresol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with cresol should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of cresol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of cresol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with cresol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cresol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cresol may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for cresol

Operations	Controls
During use in the manufacture of antiseptics and disinfectants, phosphate esters, antioxidants, resins, herbicides, perfumes, explosives, and photographic developers	Process enclosure, general dilution ventilation, personal protective equipment
During use as a solvent and as an engine and metal cleaner; during use in the textile industry	Process enclosure, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cresol, an eyewash fountain should be provided within the immediate work area for emergency use.

If cresol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to cresol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If cresol gets on the skin, wash it immediately with soap and water. If cresol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If cresol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing cresol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from cresol vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing cresol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Cresol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing cresol may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cresol (all isomers)

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 23 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) in combination with a dust and mist filter
	Any supplied-air respirator
	Any self-contained breathing apparatus
Less than or equal to 57.5 ppm	Any supplied-air respirator operated in a continuous flow mode
	Any powered air-purifying respirator with organic vapor cartridge(s) in combination with a dust and mist filter
Less than or equal to 115 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) in combination with a high-efficiency particulate filter
	Any supplied-air respirator with a full facepiece
	Any self-contained breathing apparatus with a full facepiece
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter (substance reported to cause eye irritation or damage—may require eye protection)
	Any supplied-air respirator with a tight-fitting facepiece operated in a continuous flow mode (substance reported to cause eye damage—may require eye protection)
Less than or equal to 250 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 250 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 2.3 ppm (10 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRESOL, ALL ISOMERS

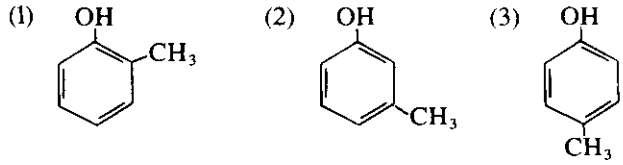
INTRODUCTION

This guideline summarizes pertinent information about the three isomers of cresol (ortho-, meta-, and para-cresol) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines. Throughout this guideline, the term "cresol" refers to any of the three isomers.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Formula:** C_7H_8O
- **Structure:**



- **Synonyms:** (1) o-Cresol; 2-cresol; o-cresylic acid; 1-hydroxy-2-methylbenzene; o-hydroxy toluene;
(2) m-Cresol; 3-cresol; m-cresylic acid; 1-hydroxy-3-methylbenzene; m-hydroxy toluene; 3-hydroxy toluene;
(3) p-Cresol; 4-cresol; p-cresylic acid; 1-hydroxy-4-methylbenzene; p-hydroxy toluene; 4-hydroxy toluene

- **Identifiers:** (1) CAS 95-48-7; RTECS G06300000; DOT 2076; (2) CAS 108-39-4; RTECS G06125000; DOT 2076; (3) CAS 106-44-5; RTECS G06475000; DOT 2076; DOT label required for all isomers: "Poison"

- **Appearance and odor:** Colorless crystals or liquid with an odor like phenol or creosote

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Physical data**

1. Molecular weight: 108.13
2. Boiling point (at 760 mmHg): (1) 191°C (376°F); (2) 202.7°C (397°F); (3) 201.9°C (395°F)
3. Specific gravity (water = 1): (1) 1.048; (2) 1.034; (3) 1.035
4. Vapor density (air = 1 at boiling point of cresol): 3.72
5. Melting point: (1) 30.9°C (87.8°F); (2) 12.0°C (49°F); (3) 34.8°C (95°F)
6. Vapor pressure at 25°C (77°F): (1) 0.25 mmHg; (2) 0.15 mmHg; (3) 0.11 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): (1) 2.5; (2) 2.2; (3) 1.9
8. Evaporation rate (butyl acetate = 1): (1) 0.025; (2) 0.015; (3) 0.011
9. Saturation concentration in air (approximate) at 25°C (77°F): (1) 0.03% (300 ppm); (2) 0.02% (200 ppm); (3) 0.014% (140 ppm)
10. Ionization potential: (1) 8.93 eV; (2) 8.98 eV; (3) 8.97 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents, alkalies, and heat.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and formaldehyde) may be released in a fire involving cresol.
3. Caution: Liquid cresol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: (1) 81.1°C (178°F) (closed cup); (2) 86.1°C (187°F) (closed cup); (3) 86.1°C (187°F) (closed cup)
2. Autoignition temperature: (1) 559°C (1040°F); (2) 626°C (1158°F); (3) 559°C (1040°F)
3. Flammable limits in air, % by volume: (1) Lower, 1.4 at 149°C (300°F); upper, not available; (2) lower, 1.1 at 150°C (302°F); upper, not available; (3) lower, 1.1 at 150°C (302°F); upper, not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

• **Warning properties**

1. Odor threshold: Less than 1 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, cresol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, cresol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cresol is 5 parts of cresol per million parts of air (ppm) [22 milligrams of cresol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes. The NIOSH REL is 2.3 ppm (10 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (22 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cresol (all isomers)

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	5	22
NIOSH REL TWA	2.3	10
ACGIH TLV® TWA (Skin)	5	22

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Cresol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**

1. *Effects on animals:* In rats and rabbits, acute dermal absorption of cresol caused tremors, convulsions, fluid in the lungs, liver injury, and kidney inflammation; oral administration caused gastrointestinal tract inflammation, pneumonia, injury to the liver and kidneys, convulsions, and coma. Chronic inhalation of cresol by rats and mice produced inflammation and fluid accumulation in the airways, damage to the bone marrow, and degeneration of cells in the brain.
2. *Effects on humans:* Acute exposure to cresol has caused alterations in brain function and death due to respiratory failure. Repeated exposure by any route has produced nervous disorders, fluid in the lungs, and death due to severe damage to the liver, kidneys, pancreas, or spleen.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to cresol can cause muscular weakness, nausea, vomiting, abdominal pain, headache, dizziness, dimness of vision, ringing in the ears, weak pulse, rapid and labored breathing, fainting, and mental confusion and depression. Skin irritation and burns can also occur. Eye contact with cresol can cause extensive damage and blindness.
2. *Long-term (chronic):* Exposure to cresol can cause difficulty in swallowing, vomiting, salivation, loss of appetite, and diarrhea. Skin eruptions, rash, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to cresol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and respiratory and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cresol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include historical and physical or laboratory findings consistent with chronic diseases of the skin or liver. In addition to the medical interview and physical examination, the means to identify these conditions may include serologic screening tests of liver function and markers for hepatitis A or B infection.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to cresol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity or physiologic function of the eyes, skin, liver, kidneys, and respiratory and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. Liver function tests should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at time of job transfer or termination**
The medical, environmental, and occupational history interviews, the physical examination, the selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to cresol may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**
Acute and delayed-onset SHE's include toxic hepatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**
Measurements to determine worker exposure to cresol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

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Where there is any possibility of a worker's eyes being exposed to cresol, an eyewash fountain should be provided within the immediate work area for emergency use.

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2. Ventilate area of spill or leak.
3. For small quantities of liquids containing cresol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from cresol vapors. Burn the paper in a suitable location away from combustible materials.
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Table 3.—Respiratory protection for cresol (all isomers)

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 23 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) in combination with a dust and mist filter
	Any supplied-air respirator
	Any self-contained breathing apparatus
Less than or equal to 57.5 ppm	Any supplied-air respirator operated in a continuous flow mode
	Any powered air-purifying respirator with organic vapor cartridge(s) in combination with a dust and mist filter
Less than or equal to 115 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) in combination with a high-efficiency particulate filter
	Any supplied-air respirator with a full facepiece
	Any self-contained breathing apparatus with a full facepiece
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter (substance reported to cause eye irritation or damage—may require eye protection)
	Any supplied-air respirator with a tight-fitting facepiece operated in a continuous flow mode (substance reported to cause eye damage—may require eye protection)
Less than or equal to 250 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 250 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 2.3 ppm (10 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRESOL, ALL ISOMERS

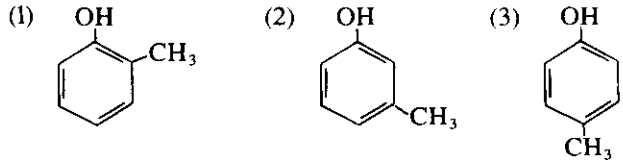
INTRODUCTION

This guideline summarizes pertinent information about the three isomers of cresol (ortho-, meta-, and para-cresol) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines. Throughout this guideline, the term "cresol" refers to any of the three isomers.

SUBSTANCE IDENTIFICATION

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Formula:** C_7H_8O
- **Structure:**



- **Synonyms:** (1) o-Cresol; 2-cresol; o-cresylic acid; 1-hydroxy-2-methylbenzene; o-hydroxy toluene;
(2) m-Cresol; 3-cresol; m-cresylic acid; 1-hydroxy-3-methylbenzene; m-hydroxy toluene; 3-hydroxy toluene;
(3) p-Cresol; 4-cresol; p-cresylic acid; 1-hydroxy-4-methylbenzene; p-hydroxy toluene; 4-hydroxy toluene

- **Identifiers:** (1) CAS 95-48-7; RTECS G06300000; DOT 2076; (2) CAS 108-39-4; RTECS G06125000; DOT 2076; (3) CAS 106-44-5; RTECS G06475000; DOT 2076; DOT label required for all isomers: "Poison"

- **Appearance and odor:** Colorless crystals or liquid with an odor like phenol or creosote

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for the three isomers of cresol: (1) ortho; (2) meta; (3) para. If unspecified, data apply to all three isomers.

- **Physical data**

1. Molecular weight: 108.13
2. Boiling point (at 760 mmHg): (1) 191°C (376°F); (2) 202.7°C (397°F); (3) 201.9°C (395°F)
3. Specific gravity (water = 1): (1) 1.048; (2) 1.034; (3) 1.035
4. Vapor density (air = 1 at boiling point of cresol): 3.72
5. Melting point: (1) 30.9°C (87.8°F); (2) 12.0°C (49°F); (3) 34.8°C (95°F)
6. Vapor pressure at 25°C (77°F): (1) 0.25 mmHg; (2) 0.15 mmHg; (3) 0.11 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): (1) 2.5; (2) 2.2; (3) 1.9
8. Evaporation rate (butyl acetate = 1): (1) 0.025; (2) 0.015; (3) 0.011
9. Saturation concentration in air (approximate) at 25°C (77°F): (1) 0.03% (300 ppm); (2) 0.02% (200 ppm); (3) 0.014% (140 ppm)
10. Ionization potential: (1) 8.93 eV; (2) 8.98 eV; (3) 8.97 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents, alkalies, and heat.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and formaldehyde) may be released in a fire involving cresol.
3. Caution: Liquid cresol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: (1) 81.1°C (178°F) (closed cup); (2) 86.1°C (187°F) (closed cup); (3) 86.1°C (187°F) (closed cup)
2. Autoignition temperature: (1) 559°C (1040°F); (2) 626°C (1158°F); (3) 559°C (1040°F)
3. Flammable limits in air, % by volume: (1) Lower, 1.4 at 149°C (300°F); upper, not available; (2) lower, 1.1 at 150°C (302°F); upper, not available; (3) lower, 1.1 at 150°C (302°F); upper, not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

• **Warning properties**

1. Odor threshold: Less than 1 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, cresol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, cresol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cresol is 5 parts of cresol per million parts of air (ppm) [22 milligrams of cresol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes. The NIOSH REL is 2.3 ppm (10 mg/m^3) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 ppm (22 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for cresol (all isomers)

	Exposure limits	
	ppm	mg/m^3
OSHA PEL TWA (Skin)*	5	22
NIOSH REL TWA	2.3	10
ACGIH TLV® TWA (Skin)	5	22

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Cresol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**

1. *Effects on animals:* In rats and rabbits, acute dermal absorption of cresol caused tremors, convulsions, fluid in the lungs, liver injury, and kidney inflammation; oral administration caused gastrointestinal tract inflammation, pneumonia, injury to the liver and kidneys, convulsions, and coma. Chronic inhalation of cresol by rats and mice produced inflammation and fluid accumulation in the airways, damage to the bone marrow, and degeneration of cells in the brain.
2. *Effects on humans:* Acute exposure to cresol has caused alterations in brain function and death due to respiratory failure. Repeated exposure by any route has produced nervous disorders, fluid in the lungs, and death due to severe damage to the liver, kidneys, pancreas, or spleen.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to cresol can cause muscular weakness, nausea, vomiting, abdominal pain, headache, dizziness, dimness of vision, ringing in the ears, weak pulse, rapid and labored breathing, fainting, and mental confusion and depression. Skin irritation and burns can also occur. Eye contact with cresol can cause extensive damage and blindness.
2. *Long-term (chronic):* Exposure to cresol can cause difficulty in swallowing, vomiting, salivation, loss of appetite, and diarrhea. Skin eruptions, rash, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**

Prior to placing a worker in a job with a potential for exposure to cresol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and respiratory and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cresol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include historical and physical or laboratory findings consistent with chronic diseases of the skin or liver. In addition to the medical interview and physical examination, the means to identify these conditions may include serologic screening tests of liver function and markers for hepatitis A or B infection.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to cresol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity or physiologic function of the eyes, skin, liver, kidneys, and respiratory and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. Liver function tests should be used and interpreted according to standardized epidemiologic procedures and evaluation criteria.

The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at time of job transfer or termination**
The medical, environmental, and occupational history interviews, the physical examination, the selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to cresol may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**
Acute and delayed-onset SHE's include toxic hepatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**
Measurements to determine worker exposure to cresol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**
Sampling and analysis may be performed by collecting cresol with silica gel tubes followed by desorption with acetone and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure cresol may also be used if available. A detailed sampling and analytical method for cresol may be found in the *NIOSH Manual of Analytical Methods* (method number 2001).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with cresol.

Workers should be provided with and required to use dust- and splash-proof safety goggles where cresol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with cresol should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of cresol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of cresol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with cresol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cresol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cresol may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for cresol

Operations	Controls
During use in the manufacture of antiseptics and disinfectants, phosphate esters, antioxidants, resins, herbicides, perfumes, explosives, and photographic developers	Process enclosure, general dilution ventilation, personal protective equipment
During use as a solvent and as an engine and metal cleaner; during use in the textile industry	Process enclosure, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cresol, an eyewash fountain should be provided within the immediate work area for emergency use.

If cresol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to cresol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If cresol gets on the skin, wash it immediately with soap and water. If cresol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If cresol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing cresol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from cresol vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing cresol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Cresol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing cresol may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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	Any supplied-air respirator
	Any self-contained breathing apparatus
Less than or equal to 57.5 ppm	Any supplied-air respirator operated in a continuous flow mode
	Any powered air-purifying respirator with organic vapor cartridge(s) in combination with a dust and mist filter
Less than or equal to 115 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s) in combination with a high-efficiency particulate filter
	Any supplied-air respirator with a full facepiece
	Any self-contained breathing apparatus with a full facepiece
	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any powered air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter (substance reported to cause eye irritation or damage—may require eye protection)
	Any supplied-air respirator with a tight-fitting facepiece operated in a continuous flow mode (substance reported to cause eye damage—may require eye protection)
Less than or equal to 250 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 250 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 2.3 ppm (10 mg/m^3) (TWA).

Occupational Health Guideline for Crotonaldehyde

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CH=CHCHO$
- Synonyms: Beta-methylacrolein; propylene aldehyde; crotonic aldehyde; 2-butenal
- Appearance and odor: Colorless to straw-colored liquid with an irritating, pungent, and suffocating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for crotonaldehyde is 2 parts of crotonaldehyde per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of crotonaldehyde per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Crotonaldehyde can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Crotonaldehyde causes irritation of the eyes, nose, and throat. It may also cause an irritation of the skin and difficulty in breathing which may occur several hours after exposure.

2. Long-term Exposure: None known

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to crotonaldehyde.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to crotonaldehyde at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from crotonaldehyde exposure.

—Chronic respiratory disease: Crotonaldehyde causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of crotonaldehyde might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Crotonaldehyde is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Crotonaldehyde vapor irritates the eyes and respiratory tract. Rats did not survive exposure to 1650 ppm for 10 minutes; there was respiratory distress, an excitatory stage, and terminal convulsions; autopsy revealed bronchiolar damage. Pulmonary edema has also been observed in rats dead of exposure to 1500 ppm for 30 minutes. Human subjects exposed to 45 ppm for a few seconds experienced conjunctival irritation; at 15 ppm there was no eye discomfort. The liquid when placed in the eyes of rabbits caused severe injury. In a series of eight cases of corneal injury from industrial exposure to crotonaldehyde, healing was complete in 48 hours; the severity of exposure was not specified. A case of apparent sensitization of undetermined nature to crotonaldehyde has been reported in a laboratory worker.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 70.1

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. Boiling point (760 mm Hg): 102 C (216 F)
3. Specific gravity (water = 1): 0.85
4. Vapor density (air = 1 at boiling point of crotonaldehyde): 2.4
5. Melting point: −75 C (−103 F)
6. Vapor pressure at 20 C (68 F): 30 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 15.5
8. Evaporation rate (butyl acetate = 1): 2.7

• **Reactivity**

1. Conditions contributing to instability: Heat may cause polymerization to occur and containers to burst.
2. Incompatibilities: Contact with caustics, ammonia, organic amines, and mineral acids may cause violent polymerization to occur. Contact with strong oxidizers may cause fires and explosions. Crotonaldehyde is readily converted by oxygen to peroxides and acids.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving crotonaldehyde.
4. Special precautions: Liquid crotonaldehyde will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 12.8 C (55 F) (closed cup)
2. Autoignition temperature: 232 C (450 F)
3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 15.5
4. Extinguishant: Carbon dioxide, dry chemical, alcohol foam

• **Warning properties**

1. Odor Threshold: Stern and May report odor thresholds for crotonaldehyde of 0.062 and 0.035 ppm, respectively.
2. Eye Irritation Level: Both Grant and the *Documentation of TLV's* report that "humans have experienced "considerable eye discomfort" at 45 ppm for a brief exposure (a few seconds). Humans did not experience eye irritation during an exposure of a few seconds to 15 ppm. The threshold of eye irritation is not given, however.
3. Other Information: According to the *Documentation of TLV's*, crotonaldehyde is also a respiratory tract irritant. The threshold limit was recommended "to prevent irritation of eyes and respiratory passages."
4. Evaluation of Warning Properties: Since the odor threshold of crotonaldehyde is below the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for crotonaldehyde is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid crotonaldehyde or liquids containing crotonaldehyde, where skin contact may occur.

• Clothing wet with liquid crotonaldehyde or liquids containing crotonaldehyde should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of crotonaldehyde from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the crotonaldehyde, the person performing the operation should be informed of crotonaldehyde's hazardous properties.

• Where exposure of an employee's body to liquid crotonaldehyde or liquids containing crotonaldehyde may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Any clothing which becomes wet with and non-impervious clothing which becomes contaminated with crotonaldehyde should be removed immediately and not reworn until the crotonaldehyde is removed from the clothing.

• Employees should be provided with and required to

use splash-proof safety goggles where there is any possibility of liquid crotonaldehyde or liquids containing crotonaldehyde contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid crotonaldehyde or liquids containing more than 1% of crotonaldehyde by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with crotonaldehyde should be immediately washed or showered to remove any crotonaldehyde.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to crotonaldehyde may occur and control methods which may be effective in each case:

Operation	Controls
Use an an intermdediate in manufacture of butyl alcohol; use in polymer technology as a reaction medium, formulator, adhesive, antioxidant, corrosion inhibitor, and stabilizer	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis in manufacture of dyestuffs, sedatives, pesticides, and flavoring agents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for purification of mineral and lubricating oils; use during manufacture of surface active agents as bactericides for petroleum well fluids, metal brighteners, and leather/paper sizing materials	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture as warning agent in fuel gases for locating breaks and leaks in pipes; use in leather tanning and preparation of tanning materials	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of rubber and rubber antioxidants and accelerators; use in manufacture of chemical warfare agents; use in photographic emulsion as a hardening agent for gelatin	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid crotonaldehyde or liquids containing crotonaldehyde get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid crotonaldehyde or liquids containing crotonaldehyde get on the skin, immediately flush the contaminated skin with water. If liquid crotonaldehyde or liquids containing crotonaldehyde soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of crotonaldehyde, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When crotonaldehyde has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If crotonaldehyde or liquids containing crotonaldehyde are spilled or leaked, the following steps should be take

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Liquid crotonaldehyde should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of crotonaldehyde vapors are permitted.

• Waste disposal method:

Crotonaldehyde may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR CROTONALDEHYDE

Condition	Minimum Respiratory Protection* Required Above 2 ppm
Vapor Concentration	
100 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
400 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 400 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRUFOMATE

INTRODUCTION

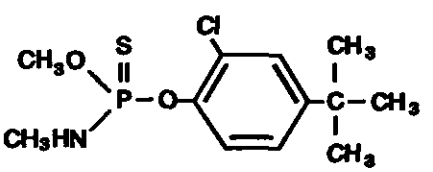
This guideline summarizes pertinent information about crufomate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{19}ClNO_3P$

- **Structure**



- **Synonyms**

Amidofos; 4-tert-butyl-2-chlorophenyl methyl methylphosphoramidate; Dowco 132; Montrel; o-methyl-o-2-chloro-4-tert-butylphenyl N-methylamidophosphate; Ruelene

- **Identifiers**

1. CAS No.: 299-86-5
2. RTECS No.: TB3850000
3. DOT UN: 2765 55 (phenoxy pesticides, solid, toxic, n.o.s.)
4. DOT label: Poison or St. Andrew's Cross (depending on quantity shipped)

- **Appearance and odor**

Crufomate is a white, crystalline solid in pure form; the commercial product is a yellow oil. Crufomate is an organophosphorus pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data

1. Molecular weight: 291.7
2. Boiling point (0.01 mm Hg): 117° to 118°C (242.6° to 244.4°F)
3. Specific gravity (water = 1): 1.2 at 70°C (158°F)
4. Vapor density: Not applicable
5. Melting point: 60° to 60.5°C (140° to 141°F) (pure); 58.7°C (137.7°F) (92%, technical grade)

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6. Vapor pressure at 117°C (242.6°F): 0.01 mm Hg

7. Solubility: Practically insoluble in water and light petroleum; soluble in benzene, alcohol, ethyl ether, cyclohexane, carbon tetrachloride, and acetonitrile.

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Heat, sparks, open flame, strong alkalies, and strong acids. Crufomate is unstable over long periods of time, in water preparations, and at temperatures above 60°C (140°F).

2. Incompatibilities: Crufomate decomposes in strongly alkaline (greater than pH 7) and strongly acidic media.

3. Hazardous decomposition products: Toxic gases (such as oxides of phosphorus and nitrogen, and chlorine) may be released in a fire involving crufomate.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to crufomate.

1. Flash point: 41.1° to 60°C (106° to 140°F), depending on the formulation

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or standard foam for small fires. Water spray, fog, or standard foam is recommended to fight large fires involving crufomate.

Fires involving crufomate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of crufomate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving crufomate. Chemical protective clothing that is specifically recommended for crufomate may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving crufomate.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for crufomate [29 CFR 1910.1000, Table Z- 1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 20 mg/m^3 as a 15-min short-term exposure limit (STEL). A STEL is a 15-min TWA concentration that should not be exceeded at any time during a workday [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned crufomate a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of neurotoxicity and cholinesterase inhibition. The ACGIH limit is based on the risk of cholinesterase inhibition associated with exposure to crufomate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to crufomate can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, crufomate is an inhibitor of plasma and erythrocyte cholinesterase.

Application of crufomate to the eye of rabbits as undiluted or 10% solutions resulted in corneal cloudiness and conjunctival irritation, along with slight pain [Clayton and Clayton 1982; ACGIH 1991]. Crufomate produced slight erythema when applied undiluted or as a 10% solution to the abraded or intact skin of the rabbit [Clayton and Clayton 1982; ACGIH 1991]. The dermal LD_{50} in rabbits is 2,000 mg/kg [NIOSH 1992b]. The lowest toxic inhalation dose in rats is 12 mg/m^3 for 4 hr [NIOSH 1992b]. The oral LD_{50} is 460 mg/kg in rats, 400 mg/kg in rabbits, and 1,000 mg/kg in guinea pigs [NIOSH 1992b]. Dogs fed 250 ppm crufomate in the diet for 75 days exhibited depression of blood cholinesterase and slight liver morphological changes; no effects were observed in dogs given dietary doses of 40 or 125 ppm [Clayton and Clayton 1982]. In 90-day dietary studies in rats, blood and/or brain cholinesterase levels were depressed 40% to 60% as compared with levels in untreated controls when doses of 30 to 1,000 ppm (1.5 to 50 mg/kg/day) were administered; no other adverse effects were observed in these animals [Clayton and Clayton 1982]. Rats fed 1,000 ppm (50 mg/kg/day) for 2 years showed marked cholinesterase inhibition, growth retardation, atrophy of the muscles of the hind limbs, and slight degeneration of the sciatic nerve; after 12, 18, or 24 months on this regimen, there was a 50% reduction in testes weights, reflecting degeneration and atrophy of the seminiferous tubules [Clayton and Clayton 1982]. No teratologic or reproductive effects were seen in male and female rats fed up to 500 ppm crufomate (25 mg/kg/day) for three generations [Clayton and Clayton 1982]. In female mice treated dermally with 50 or 100 mg/kg crufomate on days 35 and 21 before mating, the lower dose prolonged the gestation period and decreased the index of lactation and the higher dose reduced conception rate, litter size, and lactation index and decreased fetal body weight [NLM 1992].

2. *Effects on Humans:* In humans, crufomate is a moderately potent cholinesterase inhibitor.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute overexposure to crufomate by the oral route may cause severe gastrointestinal effects such as cramps, diarrhea, nausea, and anorexia. Acute inhalation exposure can cause wheezing, difficult breathing, blurred vision, and tearing. Dermal exposure causes localized twitching and sweating. Severe overexposure by any route can cause respiratory paralysis, coma, and death.

2. *Chronic exposure:* Continued low-level exposure to crufomate may lead to acetylcholine buildup, causing the signs and symptoms of systemic poisoning described above for acute overexposure.

- **Emergency procedures**

WARNING!

Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns and skin corrosion may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air immediately. Have victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if crufomate or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve crufomate and may result in worker exposures to this substance:

—Manufacture of crufomate and crufomate-containing pesticides

—Formulation and application of crufomate and crufomate-containing pesticides

—Use as a selective insecticide against cattle grubs, horn flies, and lice

The following methods are effective in controlling worker exposures to crufomate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to crufomate, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the blood. A pre-exposure plasma and red blood cell cholinesterase activity baseline should also be established.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to crufomate at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration

of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reduced plasma and red blood cell cholinesterase activity levels.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to crufomate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of crufomate on the levels of plasma or red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Absorption of crufomate can be confirmed by analysis of urine for its metabolite, crufomate phenol. However, correlations between airborne and urinary levels of crufomate and its metabolite have not been established. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophosphorus compounds such as crufomate. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for crufomate (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne crufomate is determined by using an OSHA Versatile Sampler (OVS-2) with a 13 mm XAD-2 tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method is described in OSHA's Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If crufomate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with crufomate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of crufomate.

A worker who handles crufomate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where crufomate or a solution containing crufomate is handled, processed, or stored.

STORAGE

Crufomate should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Crufomate is unstable over long periods of time in water preparations and at temperatures above 60°C (140°F). Containers of crufomate must be stacked in a manner that permits free circulation of air below and inside the pile of containers. Containers of crufomate should be protected from physical damage and should be stored separately from strong acids, strong alkalies, heat, sparks, and open flame. Because containers that formerly contained crufomate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving crufomate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Water spray may be used to reduce vapors.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the crufomate for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Crufomate is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of crufomate; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of crufomate emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although crufomate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of crufomate exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory pro-

tection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with crufomate. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to crufomate permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have demonstrated some resistance to permeation by these compounds: a laminate of Viton and neoprene, or a laminate of butyl rubber and neoprene. Since specific test data are not available for crufomate, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to crufomate.

If crufomate is dissolved an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which crufomate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with crufomate.

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Occupational Health Guideline for Cumene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5C_3H_7$
- Synonyms: Isopropylbenzene; 2-phenylpropane; cumol
- Appearance and odor: Colorless liquid with a sharp, penetrating, and aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cumene is 50 parts of cumene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 245 milligrams of cumene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cumene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Cumene may cause irritation of the skin and eyes. It may also cause dizziness, drowsiness, slight incoordination, and unconsciousness.

2. Long-term Exposure: Prolonged or repeated exposure to cumene may cause skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cumene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cumene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cumene exposure.

—Kidney disease: Although cumene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cumene might cause exacerbation of symptoms due to its irritant properties or pyschic reflex bronchospasm.

—Liver disease: Although cumene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Skin disease: Cumene is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The main toxic effect of cumene is irritation of the eyes, skin, and upper respiratory tract. Narcosis has been reported to occur in animals on high exposure. There are no reports of systemic effects in man as a result of industrial exposure. Chronic exposure of rats above 500 ppm causes congestion of lungs, liver, and kidneys, but no bone marrow changes.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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National Institute for Occupational Safety and Health

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Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 120
  2. Boiling point (760 mm Hg): 152 C (306 F)
  3. Specific gravity (water = 1): 0.86
  4. Vapor density (air = 1 at boiling point of cumene): 4.14
  5. Melting point: −96 C (−141 F)
  6. Vapor pressure at 20 C (68 F): 8 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Very low
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cumene.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 44 C (111 F) (closed cup)
  2. Autoignition temperature: 425 C (797 F)
  3. Flammable limits in air, % by volume: Lower: 0.9; Upper: 6.5
  4. Extinguishant: Water spray, dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: The AIHA *Hygienic Guide* and the ILO both report that the odor of cumene is detectable at very low levels. May reports an odor threshold for cumene of 1.2 ppm.
  2. Eye Irritation Level: The *Documentation of TLV's* notes that cumene is an eye irritant, but the concentrations producing irritation are not given.
  3. Evaluation of Warning Properties: Since the odor threshold of cumene is below the permissible exposure limit, cumene is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cumene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure cumene may be used. An analytical method for cumene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid cumene.
- Clothing wet with liquid cumene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cumene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cumene, the person performing the operation should be informed of cumene's hazardous properties.
- Non-impervious clothing which becomes wet with liquid cumene should be removed promptly and not reworn until the cumene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid cumene may contact the eyes.

SANITATION

- Skin that becomes wet with liquid cumene should be promptly washed or showered with soap or mild detergent and water to remove any cumene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cumene may occur and control methods which may be effective in each case:

Operation	Controls
Use during organic synthesis, particularly the cumene route to phenol and 2-methyl styrene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a constituent of solvents in 150 to 160 C boiling point; use during application of lacquers, paints, and enamels as thinner	General dilution ventilation; personal protective equipment
Use in petroleum distillates either alone or in solvent formulation and surface coating processes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during mixing and blending of fuels, especially aviation	General dilution ventilation; personal protective equipment
Liberation during petroleum refining processes; during production of styrene by cracking	Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If cumene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If cumene gets on the skin, promptly flush the contaminated skin with water. If cumene soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of cumene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If cumene has been swallowed, do not induce vomiting. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If cumene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid. Cumene liquid should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Cumene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid.

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RESPIRATORY PROTECTION FOR CUMENE

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).** Any supplied-air respirator.** Any self-contained breathing apparatus.**
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 8000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs at this level, a full facepiece respirator should be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYANOGEN

INTRODUCTION

This guideline summarizes pertinent information about cyanogen for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $(CN)_2$

- **Synonyms**

  Carbon nitride, dicyan, dicyanogen, ethane dinitrile, nitriloacetonitrile, oxalic acid dinitrile, oxalic nitrile, oxalonitrile, oxalyl cyanide, prussite

- Identifiers

  1. CAS No.: 460-19-5
  2. RTECS No.: GT1925000
  3. DOT UN: 1026 18
  4. DOT label: Poison Gas; Flammable Gas

- **Appearance and odor**

  Cyanogen is a highly flammable, colorless gas with a pungent, penetrating, almond-like odor; this substance is shipped as a liquefied gas under its own vapor pressure. The odor threshold is reported to be 250 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 52.04
  2. Boiling point (760 mm Hg): -21.17°C (-6.1°F)
  3. Specific gravity (for the liquid) (water = 1): 0.95 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyanogen): 1.8
  5. Melting point: -27.9°C (-18.2°F)
  6. Vapor pressure at 21°C (69.9°F): 3,868.4 mm Hg
  7. Solubility: Soluble in water, alcohol, and ether
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, shock, and direct sunlight

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2. Incompatibilities: Contact of cyanogen with acids or their vapors, water, liquid oxygen, or oxidizers (such as chlorine, fluorine, or bromine) causes explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as cyanide, hydrogen cyanide, carbon monoxide, and oxides of nitrogen) may be released in a fire involving cyanogen.

4. Special precautions: Cyanogen is denser than air and can collect in enclosed spaces. It can flow along the surface, reach distant, low-lying sources of ignition, and flash back.

Flammability

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to cyanogen.

1. Flash point: Cyanogen has a wide range of explosiveness.

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 6.6; upper, 32

4. Extinguishant: Let the fire burn unless the leak can be stopped immediately. Use water spray, fog, or standard foam to fight large fires involving cyanogen. Water may be used to cool fire-exposed containers and to protect persons attempting to stop the leak.

Fires involving cyanogen should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Cyanogen is heavier than air and may travel to a source of ignition and flash back. Containers of cyanogen may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyanogen. Chemical protective clothing that is specifically recommended for cyanogen may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing may provide limited protection against fires involving cyanogen.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyanogen [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (20 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyanogen a threshold limit value (TLV) of 10 ppm (21 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and respiratory irritation associated with cyanogen exposure. The ACGIH limit is based on the risk of irritant and systemic effects associated with exposure to cyanogen.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyanogen can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Cyanogen is a highly toxic gas that causes severe irritation, respiratory distress, and death on acute exposure. Rabbits survived dermal exposure to 10,000 ppm for 8 hours without apparent systemic effects [McNerney and Schrenk 1960]. The

LC_{50} in rats is 350 ppm for 1 hr [NIOSH 1990]. Acutely poisoned animals showed signs of respiratory distress and severe eye irritation before death [NIOSH 1990]. Monkeys and rats exposed for 6 hr/day, 5 days/week to 11 or 25 ppm of cyanogen for 6 months showed no hematologic, clinical, or histopathological changes attributable to exposure [NLM 1992].

2. *Effects on Humans:* Cyanogen causes cellular hypoxia in humans; in lethal amounts, it causes respiratory and central nervous system stimulation, followed by headache, vertigo, agitation followed by combative behavior, coma, convulsions, respiratory arrest, and death [NLM 1992]. Cyanogen reacts readily with cytochrome oxidase in mitochondria which inhibits tissue oxidation resulting in cytotoxic hypoxia. In addition to hypoxia, exposure to cyanogen causes eye, nose, and upper respiratory tract irritation. Exposure to a concentration of 16 ppm for 6 to 8 min caused irritation, but exposure to 8 ppm for the same interval caused no irritation [McNerney and Schrenk 1960].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyanogen may cause pain, redness, and tearing of the eyes, runny nose, and difficult breathing; if the overexposure is severe, the following signs of cyanide poisoning are seen: cherry red lips, tachypnea and hyperpnea (followed by bradycardia), headache, vertigo, agitation, behavioral changes, and convulsions.

2. *Chronic exposure:* The signs and symptoms of chronic overexposure to cyanogen include those of thyroid dysfunction: dizziness, loss of appetite, and weight loss.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL

The following operations may involve cyanogen and may result in worker exposures to this substance:

—Use as an intermediate in organic synthesis

—Use as a fumigant

—Use for welding and cutting heat-resistant metals

—Use as a rocket and missile propellant

The following methods are effective in controlling worker exposures to cyanogen, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cyanogen, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and thyroid.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyanogen at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system or thyroid.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyanogen exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyanogen on the respiratory system or thyroid. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Thiocyanate, a metabolite of cyanide, can be measured in the plasma and urine of exposed individuals. However, the levels of thiocyanate in these body fluids that correspond to airborne concentrations of cyanogen have not been determined. Therefore, no biological monitoring test acceptable for routine use has yet been developed for cyanogen.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyanogen is determined

by using a coated XAD-2 tube (150/75-mg sections, 20/60 mesh) coated with 10% (w/w) 2-(hydroxymethyl) piperidine. Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 12 liters is collected. Analysis is conducted by gas chromatography using a nitrogen phosphorus detector. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cyanogen contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cyanogen should be removed immediately.

A worker who handles cyanogen should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyanogen is handled, processed, or stored.

STORAGE

Cyanogen should be stored in pressurized, secured, airtight containers in a cool, dry, well-ventilated area; the containers must be labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must meet requirements for a Class I flammable liquid. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Ventilation systems used in cyanogen storage areas must be maximally explosion proof. Containers of cyanogen should be protected from physical damage and should be stored separately from water, acids, acid vapors, and oxidizers. Containers should also be protected from shock, direct sunlight, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arresters. Only non sparking tools may be used to handle cyanogen. To prevent static sparks, containers should be grounded and bonded for transfers.

LEAKS

In the event of a leak involving cyanogen, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a leak:

1. Stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not get water inside the container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyanogen is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for cyanogen is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of cyanogen per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA [49 CFR 372.30] reporting the amount of cyanogen emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cyanogen is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P031. This substance has been banned from land disposal and may be treated by chemical oxidation, wet air oxidation, or incineration. Cyanogen also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyanogen exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and full-body clothing, as appropriate) should be worn to prevent any skin contact with liquid cyanogen. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyanogen permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyanogen.

Safety glasses, goggles, or face shields should be worn during operations in which cyanogen might contact the eyes. Eyewash fountains and emergency showers should

be available within the immediate work area whenever the potential exists for eye or skin contact with cyanogen. Contact lenses should not be worn if the potential exists for cyanogen exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYANOGEN CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about cyanogen chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  ClCN

- **Structure**

  N≡CCl

- **Synonyms**

  Chlorcyan; chlorine cyanide; chlorocyanide; chlorocyanogen

- **Identifiers**

  1. CAS No.: 506-77-4
  2. RTECS No.: GT2275000
  3. DOT UN: 1589 15 (for cyanogen chloride containing less than 0.9% water)
  4. DOT label: Poison gas; Flammable gas

- **Appearance and odor**

  Cyanogen chloride is a colorless gas with a pungent, penetrating odor. It is shipped in steel cylinders under its own vapor pressure as a liquefied gas. The odor threshold of cyanogen chloride is 1 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 61.5
  2. Boiling point (760 mm Hg): 13.8°C (56.8°F)
  3. Specific gravity (water = 1): 1.2 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyanogen chloride): 2.16
  5. Melting point: -6°C (21.2°F)
  6. Vapor pressure at 20°C (68°F): 1,000 to 1,010 mm Hg
  7. Solubility: Soluble in water, alcohol, ether, and all organic solvents

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Moisture, sparks, heat, or flame

2. Incompatibilities: Contact of cyanogen chloride with water, steam, acids, acid salts, or strong oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic substances (such as the oxides of nitrogen cyanide, cyanide, chloride ions, and hydrogen cyanide) may be released in a fire involving cyanogen chloride.

4. Special precautions: Crude cyanogen chloride trimerizes violently to cyanuric chloride if catalyzed by traces of hydrogen chloride or ammonium chloride.

Flammability

The National Fire Protection Association has not assigned a flammability rating to cyanogen chloride. However, the Hazardous Materials Identification System (HMIS) developed by the National Paint and Coatings Association assigns cyanogen chloride a flammability rating of 4 (severe fire hazard).

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, fog, or standard foam to fight fires involving cyanogen chloride.

Fires involving cyanogen chloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of cyanogen chloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Take care not to permit water to contact the cyanogen chloride inside the containers. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyanogen chloride. Chemical protective clothing that is specifically recommended for cyanogen chloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing may provide limited protection against fires involving cyanogen chloride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyanogen chloride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.3 ppm (0.6 mg/m^3) as a ceiling limit [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyanogen chloride a ceiling limit value of 0.3 ppm (0.75 mg/m^3) [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of severe eye and pulmonary irritation [NIOSH 1992]. The ACGIH limit is based on the risk of irritant, metabolic, and respiratory effects associated with exposure to cyanogen chloride [ACGIH 1993].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyanogen chloride can occur through inhalation, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cyanogen chloride causes eye, mucous membrane, skin, and upper respiratory tract

irritation in animals. Although experimental data on skin absorption are lacking, this substance is reported to cause systemic toxicity when absorbed through the skin in toxic amounts [NLM 1992]. The LC_{50} in rats is 5,400 mg/m^3 (2,700 ppm) for 3 min; in monkeys, it is 4,400 mg/m^3 (2,200 ppm) for 1 min; and in rabbits, it is 6,000 mg/m3 (3,000 ppm) for 7 min [NIOSH 1993]. Animals acutely poisoned with cyanogen chloride show signs of cyanide poisoning and pulmonary edema (dyspnea, bloody nasal exudate, cyanosis) before death [ACGIH 1991].

2. *Effects on Humans:* Cyanogen chloride is a severe eye, skin, mucous membrane, and upper respiratory tract irritant in humans. Exposure to cyanogen chloride also causes cellular hypoxia, as is the case with other cyanides. Exposure to concentrations of cyanogen chloride below 1 ppm (approximately 0.7 ppm) causes burning of the eyes, lacrimation, and severe blepharospasm, local skin irritation, and marked respiratory tract irritation, with hemorrhagic changes and pulmonary edema [Grant 1986; NLM 1992; ACGIH 1991]. Cyanide also interferes with the cell's ability to utilize oxygen, which leads to cellular hypoxia, headache, dizziness, and signs and symptoms that include seizures and coma. Exposure to a cyanogen chloride concentration of 48 ppm for 30 min or to a 159-ppm concentration for 10 min has caused death in humans [Clayton and Clayton 1982]. Repeated inhalation of low (not further specified) concentrations of cyanogen chloride may cause dizziness, lung congestion, loss of appetite, mental deterioration, and weight loss [NLM 1992]. Workers chronically exposed to cyanide salts during metal heat-treating operations developed enlarged thyroid glands [ACGIH 1991; NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyanogen chloride may cause burning of the eyes, tearing, and spasms of the eyelids; a bitter, burning taste followed by a feeling of constriction in the mouth; sweating, salivation, nausea, and vomiting; anxiety confusion, vertigo, giddiness, dizziness, and headache; a bright pink or brick-red coloration to the skin; difficult breathing; increased or decreased blood pressure and heart rate; seizures; and an increase in respiratory rate followed by respiratory arrest.

2. *Chronic exposure:* Chronic overexposure to cyanogen chloride may cause dizziness, lung congestion, loss of appetite, mental deterioration, weight loss, and enlargement of the thyroid.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyanogen chloride and may result in worker exposures to this substance:

—Use in organic synthesis

—Military use as a poison and tear gas

—Use as a warning agent in fumigant gases

—Use in ore refining, in the production of synthetic rubber, and as a metal cleaner

—Use in the Lonza process to produce extremely pure malononitrile

The following methods are effective in controlling worker exposures to cyanogen chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to cyanogen chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and thyroid. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyanogen chloride at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system or thyroid.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyanogen chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyanogen chloride on the respiratory system or thyroid. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Thiocyanate, a metabolite of cyanide, can be measured in the plasma and urine of exposed individuals. However, the levels of thiocyanate in these body fluids that correspond to airborne concentrations of cyanogen chloride have not been determined. Therefore, no biological monitoring test acceptable for routine use has yet been developed for cyanogen chloride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyanogen chloride is determined by using a coated XAD-2 tube (150/75-mg sections, 20/60 mesh). The coating is 10% (w/w) 2-(hydroxymethyl)piperidine. Samples are collected at a maximum flow rate of 0.2 liter/min. The sample is then treated with toluene to extract the cyanogen chloride. Analysis is conducted by gas chromatography using a nitrogen phosphorus detector. This method is described in the OSHA Computerized Information System [OSHA 1992].

PERSONAL HYGIENE

Cyanogen chloride can be absorbed through the skin in toxic amounts. Therefore, if cyanogen chloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with cyanogen chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cyanogen chloride, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles cyanogen chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyanogen chloride or a solution containing cyanogen chloride is handled, processed, or stored.

STORAGE

Cyanogen chloride gas or liquid should be stored in a cool, dry, well-ventilated area in pressurized, airtight containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Cyanogen chloride should not be exposed to direct sunlight. Containers of cyanogen chloride should be protected from shock or physical damage and should be stored separately from water, acids, acid vapors, strong oxidizing agents, heat, sparks, and open flame. Because containers that formerly contained cyanogen chloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyanogen chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Evacuate all nonessential personnel.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not put water directly on the leak or spill area.
6. Do not get water inside container.
7. For small liquid spills, flush area with flooding amounts of water.
8. For large liquid spills, build dikes far ahead of the spill to contain the cyanogen chloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Cyanogen chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

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A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

The reportable quantity for cyanogen chloride is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center *immediately* at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyanogen chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cyanogen chloride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P033. This substance has been banned from land disposal and may be treated by chemical oxidation, wet air oxidation, or incineration. Cyanogen chloride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

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- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the

requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and full-body clothing) should be worn as necessary to prevent any skin contact with cyanogen chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyanogen chloride permeation; however, butyl rubber is reported to provide no more than 1 hr of resistance against permeation by cyanogen bromide, a chemically similar substance. Since specific test data are not available for cyanogen chloride, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyanogen chloride.

If cyanogen chloride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyanogen chloride gas or liquid might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyanogen chloride. Contact lenses should not be worn if the potential exists for cyanogen chloride exposure.

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Occupational Health Guideline for Cyclohexane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6H_{12}
- Synonyms: Hexahydrobenzene; hexamethylene; benzene hexahydride
- Appearance and odor: Colorless liquid with mild, sweet odor resembling chloroform or benzene.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyclohexane is 300 parts of cyclohexane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1050 milligrams of cyclohexane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclohexane can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to cyclohexane may cause dizziness and nausea. At higher levels of exposure, a person may become unconscious. Liquid splashes of cyclohexane may iritate the eyes.

2. Long-term Exposure: Prolonged or repeated exposures can cause skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyclohexane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyclohexane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cyclohexane exposure.

—Skin disease: Cyclohexane is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although cyclohexane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclohexane might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although cyclohexane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Cyclohexane is primarily a local irritant and central nervous system depressant. The depressant effect is from exposure to conconcentrations above 12,000 ppm, while prolonged or repeated exposure to concentrations above 300 ppm produces a mild irritation of the eyes and upper respiratory tract. Aspiration causes a chemical pneumonitis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 84
  2. Boiling point (760 mm Hg): 80 C (177 F)
  3. Specific gravity (water = 1): 0.78
  4. Vapor density (air = 1 at boiling point of cyclohexane): 2.98
  5. Melting point: 6.5 C (44 F)
  6. Vapor pressure at 20 C (68 F): 95 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.01
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclohexane.
  4. Special precautions: None
- **Flammability**
  1. Flash point: −20 C (−4 F) (closed cup)
  2. Autoignition temperature: 245 C (473 F)
  3. Flammable limits in air, % by volume: Lower: 1.31; Upper: 8.35
  4. Extinguishant: Dry chemical, foam, or carbon dioxide
- **Warning properties**
  1. Odor Threshold: May reports that the odor threshold of cyclohexane is 0.41 ppm. The Manufacturing Chemists Association (MCA) reports that "the sweetish odor of cyclohexane, which resembles that of chloroform, is not adequate warning against exposure to hazardous concentrations." The AIHA *Hygienic Guide* reports similar information.
  2. Eye Irritation Level: The *Documentation of TLV's* reports that, according to Gerarde, a concentration of 300 ppm is somewhat irritating to the eyes. The MCA, however, states that even in high concentrations the vapor is not irritating to the eyes.
  3. Evaluation of Warning Properties: Since the MCA and the *Hygienic Guide* both state that the odor of cyclohexane is not sufficient warning against exposure to hazardous concentrations, and since MCA states that even high concentrations of cyclohexane do not cause eye irritation, for the purposes of this guideline, cyclohexane is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cyclohexane vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure cyclohexane may be used.

An analytical method for cyclohexane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid cyclohexane.
- Clothing wet with liquid cyclohexane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclohexane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyclohexane, the person performing the operation should be informed of cyclohexane's hazardous properties.
- Any clothing which becomes wet with liquid cyclohexane should be removed immediately and not reworn until the cyclohexane is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid cyclohexane may contact the eyes.

SANITATION

• Skin that becomes wet with cyclohexane should be promptly washed or showered with soap or mild detergent and water to remove any cyclohexane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyclohexane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent to dissolve cellulose ethers, resins, fats, waxes, oils, bitumin, and crude rubber; use in perfume manufacture; use during surface coating operations (lacquers)	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of adipic acid for production of Nylon 66 and engineering plastics	Process enclosure; local exhaust ventilation; personal protective equipment
Use during synthesis of caprolactam in Nylon 6 production	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If cyclohexane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If cyclohexane gets on the skin, promptly flush the contaminated skin with water. If cyclohexane soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of cyclohexane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If cyclohexane has been swallowed, do not induce vomiting. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If cyclohexane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid. Cyclohexane liquid should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Cyclohexane may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid.

REFERENCES

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RESPIRATORY PROTECTION FOR CYCLOHEXANE

Condition	Minimum Respiratory Protection* Required Above 300 ppm
Vapor Concentration	
3000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
10,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Cyclohexanol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_{11}OH$
- Synonyms: Hexalin; hydroxycyclohexane; hydralin; anol; hexahydrophenol; cyclohexyl alcohol
- Appearance and odor: Colorless, viscous liquid or sticky solid with a faint, camphor-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyclohexanol is 50 parts of cyclohexanol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 200 milligrams of cyclohexanol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclohexanol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to cyclohexanol may cause headache and irritation of the eyes, nose, and throat.

2. Long-term Exposure: Repeated exposure to cyclohexanol may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyclohexanol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyclohexanol at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cyclohexanol exposure.

—Skin disease: Cyclohexanol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although cyclohexanol is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although cyclohexanol is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclohexanol might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Cyclohexanol vapor has a narcotic effect at high concentrations and causes irritation of the eyes, nose, and throat. Prolonged exposure at 145 ppm resulted in minimal changes in the liver and kidneys of rabbits. Lethargy occurs in the monkey at 700 ppm, and narcosis in rabbits at 1000 ppm. The liquid defats the skin and may produce dermatitis upon prolonged or frequent contact. No chronic systemic effects have been reported in humans.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 100
  2. Boiling point (760 mm Hg): 161 C (322 F)
  3. Specific gravity (water = 1): 0.96
  4. Vapor density (air = 1 at boiling point of cyclohexanol): 3.5
  5. Melting point: 23.6 C (75 F)
  6. Vapor pressure at 20 C (68 F): 1 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 3.6
  8. Evaporation rate (butyl acetate = 1): 0.08
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclohexanol.
  4. Special precautions: Cyclohexanol will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 67.8 C (154 F (closed cup)
  2. Autoignition temperature: 300 C (572 F)
  3. Flammable limits in air, % by volume: Lower: 2.4 (calculated at flash point)
  4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical
- **Warning properties**
  1. Odor Threshold: No quantitative information is available.
  2. Irritation Levels: The *Documentation of TLV's* states that "Nelson and his associates found 100 ppm of cyclohexanol to be objectionable to the ten persons subjected to this concentration in a study of sensory response to a number of solvent vapors. In this study the individuals classified the effect of the vapor on the eyes, nose, and throat after 3 to 5 minutes' exposure as objectionable. The limit of 50 ppm was chosen to reduce objectionable irritation."
  3. Evaluation of Warning Properties: Since cyclohexanol is known to produce eye, nose, and throat irritation at a concentration only twice the permissible exposure limit, it is treated as a substance with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of cyclohexanol vapors using an adsorption tube with subsequent desorption with 2-propanol in carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure cyclohexanol may be used. An analytical method for cyclohexanol is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid or liquid cyclohexanol.
- Clothing wet with liquid cyclohexanol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclohexanol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyclohexanol, the person performing the operation should be informed of cyclohexanol's hazardous properties.
- Non-impervious clothing which becomes contaminated with solid or liquid cyclohexanol should be removed promptly and not reworn until the cyclohexanol is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where liquid or solid cyclohexanol may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid or solid cyclohexanol should be promptly washed or showered with soap or mild detergent and water to remove any cyclohexanol.
• Employees who handle liquid or solid cyclohexanol should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyclohexanol may occur and control methods which may be effective in each case:

Operation	Controls
Use during synthesis of adipic acid, primarily in production of Nylon 66	General dilution ventilation; personal protective equipment
Liberation during synthesis of caprolactam	General dilution ventilation
Use during application of surface coatings of natural and synthetic textile dyes, cotton mercerizers, paints, varnishes, lacquers, and shellacs	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in cleaning and degreasing operations	Local exhaust ventilation; personal protective equipment
Use in production of dicyclohexyl phthalate, other cyclohexyl esters, soaps, synthetic detergents, and rubber cement	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.
• **Eye Exposure**
If cyclohexanol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.
• **Skin Exposure**
If cyclohexanol gets on the skin, promptly wash the contaminated skin with water. If cyclohexanol soaks through the clothing, remove the clothing promptly and flush the skin with water. If there is skin irritation, get medical attention.
• **Breathing**
If a person breathes in large amounts of cyclohexanol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
• **Swallowing**
When cyclohexanol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.
• **Rescue**
Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
• If cyclohexanol is spilled or leaked, the following steps should be taken:
1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, mixed with ethyl alcohol, and atomized in a suitable combustion chamber.
• Waste disposal methods:
Cyclohexanol may be disposed of:
1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By mixing with ethyl alcohol and atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR CYCLOHEXANOL

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2500 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3500 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 3500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

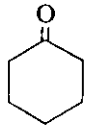
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYCLOHEXANONE

INTRODUCTION

This guideline summarizes pertinent information about cyclohexanone for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{10}O$
- **Structure:**



- **Synonyms:** Anone, hexanon, ketohexamethylene, nadone, pimelic ketone, pimelin ketone
- **Identifiers:** CAS 108-94-1; RTECS GW1050000; DOT 1915, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless to slightly yellow liquid with an odor like peppermint

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.16
2. Boiling point (at 760 mmHg): 155.6°C (312°F)
3. Specific gravity (water = 1): 0.95
4. Vapor density (air = 1 at boiling point of cyclohexanone): 3.4
5. Melting point: -47°C (-52.6°F)
6. Vapor pressure at 20°C (68°F): 2 mmHg; at 25°C (77°F), 4.5 mmHg
7. Slightly soluble in water
8. Evaporation rate (butyl acetate = 1): 0.23
9. Saturation concentration in air (approximate) at 20°C (68°F): 0.26% (2,600 ppm); at 25°C (77°F), 0.60% (6,000 ppm)
10. Ionization potential: 9.14 eV

- **Reactivity**

1. Incompatibilities: Cyclohexanone may react with oxidizing agents and nitric acid causing fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving cyclohexanone.
3. Caution: Cyclohexanone will dissolve most plastics, resins, and rubber.

- **Flammability**

1. Flash point: 43.9°C (111°F) (closed cup)
2. Autoignition temperature: 420°C (788°F)
3. Flammable limits in air, % by volume: Lower, 1.1; Upper, 9.4
4. Extinguishant: Alcohol foam, dry chemical, or carbon dioxide
5. Class II Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.88 ppm
2. Eye irritation level: 75 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, cyclohexanone can be detected at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for cyclohexanone is 50 parts of cyclohexanone per million parts of air (ppm) [200 milligrams of cyclohexanone per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 25 ppm (100 mg/m³) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 25 ppm (100 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

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National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for cyclohexanone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	50	200
NIOSH REL TWA	25	100
ACGIH TLV® TWA (Skin)	25	100

HEALTH HAZARD INFORMATION

• Routes of exposure

Cyclohexanone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

Effects on animals: Subchronic inhalation of cyclohexanone by rabbits and monkeys caused central nervous system depression and liver and kidney degeneration. Cutaneous or subcutaneous application of cyclohexanone for several days caused cataracts in guinea pigs.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to cyclohexanone can cause dizziness and unconsciousness. Irritation of the eyes, nose, and throat can also occur.
2. *Long-term (chronic):* Dermal exposure to cyclohexanone can cause dryness, irritation, and inflammation of the skin.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to cyclohexanone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and respiratory system. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to cyclohexanone at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindication to job placement, include concurrent dermatitis or a history of chronic skin disease.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to cyclohexanone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

• Sentinel health events

Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to cyclohexanone should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under cer-

tain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Method**

Sampling and analysis may be performed by collecting cyclohexanone vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure cyclohexanone may also be used if available. A detailed sampling and analytical method for cyclohexanone may be found in the *NIOSH Manual of Analytical Methods* (method number 1300).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with cyclohexanone.

Workers should be provided with and required to use splash-proof safety goggles where cyclohexanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with cyclohexanone should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclohexanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of cyclohexanone's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with cyclohexanone should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle cyclohexanone should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to cyclohexanone may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for cyclohexanone

Operations	Controls
During surface coating or spray painting of fabrics and plastics	Local exhaust ventilation, personal protective equipment
During cleaning of leathers and textiles; during degreasing of leathers and metals	Local exhaust ventilation, personal protective equipment
During use as a solvent in crude rubber, insecticides, and epoxy resins; during use as a sludge solvent in lubricating oils	Local exhaust ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

- **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to cyclohexanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If cyclohexanone gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin exposure**

Where there is any possibility of a worker's body being exposed to cyclohexanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If cyclohexanone gets on the skin, wash it immediately with soap and water. If cyclohexanone penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

- **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If cyclohexanone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing cyclohexanone, absorb on paper towels and place in an appropriate container. Place towels in a safe place (such as a fume hood) for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from cyclohexanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing cyclohexanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Cyclohexanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Cyclohexanone may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for cyclohexanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 625 ppm	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Less than or equal to 1,250 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 5,000 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 5,000 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 25 ppm (100 mg/m^3) (TWA).

Occupational Health Guideline for Cyclohexene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6H_{10}
- Synonyms: Benzene tetrahydride
- Appearance and odor: Colorless liquid with a sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyclohexene is 300 parts of cyclohexene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1015 milligrams of cyclohexene per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclohexene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to cyclohexene may cause irritation of the eyes, nose, and throat.
2. Long-term Exposure: Prolonged or repeated contact of this chemical with the skin may cause skin irritation.
3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyclohexene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyclohexene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cyclohexene exposure.

—Skin disease: Cyclohexene can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although cyclohexene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although cyclohexene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclohexene might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

While no significant toxicologic studies on cyclohexene have been reported, it is regarded as a mild respiratory irritant and central nervous system depressant, chiefly by analogy to the observed effect of chemically similar substances. No acute or chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 82
  2. Boiling point (760 mm Hg): 82.8 C (181 F)
  3. Specific gravity (water = 1): 0.8
  4. Vapor density (air = 1 at boiling point of cyclo-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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hexene): 2.8

5. Melting point: −103.7 C (−155 F)

6. Vapor pressure at 20 C (68 F): 67 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Very low

8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclohexene.

4. Special precautions: Cyclohexene will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: −12 C (10 F) (closed cup)

2. Autoignition temperature: 310 C (590 F)

3. Flammable limits in air, % by volume: Lower: 1.2; Upper: 4.8 at 100 C (212 F)

4. Extinguishant: Dry chemical, carbon dioxide, foam

• **Warning properties**

1. Odor Threshold: By analogy to cyclohexane, which has an odor threshold of 0.41 ppm according to May, the odor of cyclohexene is assumed to be below the permissible exposure limit of 300 ppm.

2. Eye Irritation Level: The *Documentation of TLV's* states that "Cook suggested 400 ppm as a TLV (for cyclohexene) on the basis of analogy to cyclohexane. This limit has subsequently been reduced to 300 ppm to provide a wider margin of safety from systemic effects and to reduce irritation."

3. Evaluation of Warning Properties: By analogy to cyclohexane, the odor threshold of cyclohexene is assumed to be below the permissible exposure limit. Cyclohexene, therefore, is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of cyclohexene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure cyclohexene may be used. An analytical method for cyclohexene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid cyclohexene.

• Clothing wet with liquid cyclohexene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclohexene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyclohexene, the person performing the operation should be informed of cyclohexene's hazardous properties.

• Any clothing which becomes wet with liquid cyclohexene should be removed immediately and not reworn until the cyclohexene is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid cyclohexene may contact the eyes.

SANITATION

• Skin that becomes wet with liquid cyclohexene should be promptly washed or showered with soap or mild detergent and water to remove any cyclohexene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyclohexene may occur and control methods which may be effective in each case:

Operation	Controls
Use in organic synthesis as a starting material or chemical intermediate	Process enclosure; local exhaust ventilation; personal protective equipment; general dilution ventilation
Use as a constituent to study catalytic reactions, mechanisms of oxidation of hydrocarbons, and reaction kinetics	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in synthesis of polymers; as a polymer modifier to control molecular weight; use as a stabilizing agent	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during catalytic hydrogenation of aromatic compounds	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If cyclohexene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If cyclohexene gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If cyclohexene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of cyclohexene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If cyclohexene has been swallowed, do not induce vomiting. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If cyclohexene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Cyclohexene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Cyclohexene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR CYCLOHEXENE

Condition	Minimum Respiratory Protection* Required Above 300 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
10,000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND GUIDELINE FOR CYCLOHEXYLAMINE

INTRODUCTION

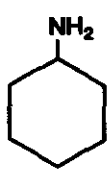
This guideline summarizes pertinent information about cyclohexylamine for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_6H_{11}NH_2$

- **Structure**



- **Synonyms**

Aminocyclohexane, aminohexahydrobenzene, CHA, cyclohexanamine, hexahydroaniline, hexahydrobenzenamine

- **Identifiers**

1. CAS No.: 108-91-8
2. RTECS No.: GX0700000
3. DOT UN: 2357 68
4. DOT label: Flammable liquid; corrosive

- **Appearance and odor**

Cyclohexylamine is a flammable, colorless or yellow liquid with a strong, fishy, amine odor. The odor threshold of cyclohexylamine is 2.6 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 99.17
2. Boiling point (760 mm Hg): 134.5°C (274.1°F)
3. Specific gravity (water = 1): 0.87 at 25°C (77°F)
4. Vapor density (air = 1 at boiling point of cyclohexylamine): 3.42
5. Melting point: -17.7°C (0.14°F)

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Occupational Safety and Health Administration

6. Vapor pressure at 20°C (68°F): 11.3 mm Hg

7. Solubility: Completely soluble in water and most organic solvents, including alcohols, ethers, ketones, esters, and chlorinated hydrocarbons; also soluble in peanut oil, mineral oil, acetone, and benzene.

8. Evaporation rate (ether = 1): 82.9

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame. Contact of the vapor with air generates an explosive mixture.

2. Incompatibilities: Contact of cyclohexylamine with oxidizers, organic compounds, acid anhydrides, acid chlorides, alkylene oxides, acids, any copper alloy, zinc, or galvanized steel may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving cyclohexylamine.

4. Special precautions: Avoid contact of the vapors with air.

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to cyclohexylamine.

1. Flash point: 31°C (88°F) (open cup)

2. Autoignition temperature: 293°C (560°F)

3. Flammable limits in air (% by volume): Lower 1.5; upper 9.4

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, or standard foam to fight fires involving cyclohexylamine. Do not use a solid stream of water because the stream will scatter and spread the fire. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving cyclohexylamine should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cyclohexylamine may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclohexylamine. Structural firefighters' protective clothing may provide limited protection against fires involving cyclohexylamine.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclohexylamine [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 10 ppm (40 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclohexylamine a threshold limit value (TLV) of 10 ppm (41 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of severe eye and skin irritation associated with exposure to cyclohexylamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclohexylamine can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cyclohexylamine is a severe irritant of the eyes, mucous membranes, and skin in animals. A single drop of a 50% aqueous solution of cyclohexylamine onto the conjunctival sac of a rabbit's eye caused complete destruction of the eye [ACGIH 1991]. When applied to the skin of rabbits, this substance caused severe skin damage [NIOSH 1990]. Although skin sensitization tests in guinea pigs yielded negative results, cyclohexylamine is believed to have weak sensitizing potential [ACGIH 1991; NJDH 1991]. The dermal LD_{50} in rabbits is 277 mg/kg [NIOSH 1990]. Fifty percent of exposed rats died after inhaling a cyclohexylamine concentration of 7,500 mg/m^3 for an unspecified time [NIOSH 1990]. Acutely poisoned animals displayed signs of severe irritation and of central nervous system effects before death [NIOSH 1990]. Rabbits, rats, and guinea pigs exposed for 7 hr/day, 5 days/week to a 1,200-ppm concentration of cyclohexylamine died after a single exposure; however, most animals exposed to a 150-ppm concentration on the same regimen survived for 10 such exposures. Before death, animals of all species exhibited signs of eye and respiratory tract irritation and developed corneal opacities [Clayton and Clayton 1981]. The oral LD_{50} is 156 mg/kg for rats and 224 mg/kg for mice [NIOSH 1990]. In rats, cyclohexylamine has caused reproductive effects in males (reduction in the number and size of litters sired) and females (reduction in pregnancy rate, number of live-born fetuses and post-natal survivors, and birthweight of offspring) [Clayton and Clayton 1981]. In experiments involving rats, mice, and dogs, cyclohexylamine has induced fetotoxic and/or paternal reproductive effects by oral, intraperitoneal, and parenteral administration [NIOSH 1990]. Cyclohexylamine has caused chromosomal breaks in a number of in-vitro test systems [IARC 1980]. Cyclohexylamine has been tested for carcinogenicity in two oral bioassays in mice and four in rats. Based on the results of this research, the International Agency for Research on Cancer (IARC) has concluded that the evidence for the carcinogenicity of cyclohexylamine in animals is inadequate [IARC 1980].

2. *Effects on Humans:* Cyclohexylamine is a severe irritant of the eyes, skin, mucous membranes, and respiratory tract in humans; it may also cause skin sensitization in some individuals. Cyclohexylamine has caused severe irritation upon contact with the skin; patch tests have shown that this substance is capable of causing skin sensitization [NIOSH 1990; Clayton and Clayton 1981]. Three workers who had been accidentally overexposed to an unspecified concentration of cyclohexylamine experienced symptoms of lightheadedness, drowsiness, anxiety, apprehension, and nausea; one acutely poisoned worker also developed slurred speech and vomited [Hathaway et al. 1991]. Human volunteers who ingested 5 grams of cyclohexylamine a day for 7 or 8 consecutive days showed no adverse effects; workers exposed to airborne concentrations of this substance in the range of 4 to 10 ppm also reported experiencing no symptoms [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyclohexylamine can cause severe irritation of the eyes, with tearing and conjunctivitis; irritation of the respiratory tract, with coughing and difficult breathing; and severe skin irritation, with burns, blisters, redness, swelling, and cell death. Acutely poisoned workers also may experience apprehension, drowsiness, lightheadedness, and vomiting.

2. *Chronic exposure:* Repeated or chronic exposure to cyclohexylamine may cause corneal opacities, dryness and cracking of the skin, and, in some individuals, skin sensitization, with itching, wheals, and redness of the affected areas.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of cyclohexylamine! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclohexylamine or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more.***

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclohexylamine and may result in worker exposures to this substance:

—Use as an intermediate in the production of cyclamate sweeteners and textile and rubber chemicals

—Use as a corrosion inhibitor in boiler feed water and oil fields and in the packaging of metal equipment

—Manufacture of dyes, insecticides, plasticizers, emulsifying agents, acid gas absorbents, and dry-cleaning soaps

The following methods are effective in controlling worker exposures to cyclohexylamine, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveil-

lance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cyclohexylamine, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory tract. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society (ATS) [1987].

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclohexylamine at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies and other findings consistent with diseases of the eyes, skin, or respiratory tract.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclohexylamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclohexylamine on the eyes, skin, or respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclohexylamine.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyclohexylamine is determined by using a silica gel tube (600/150/150-mg sections, 20/40 mesh). Samples are collected at a recommended flow rate of 0.2 liter/min until a recommended air volume of 96 liters is collected. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in Method P&CAM 221 of the *NIOSH Manual of Analytical Methods* [NIOSH 1977].

PERSONAL HYGIENE

If cyclohexylamine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with cyclohexylamine should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons

laundering the clothes should be informed of the hazardous properties of cyclohexylamine, particularly its potential to cause severe irritation of the eyes and skin.

A worker who handles cyclohexylamine should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclohexylamine or a solution containing cyclohexylamine is handled, processed, or stored.

STORAGE

Cyclohexylamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of cyclohexylamine should be protected from physical damage and should be stored separately from strong oxidizers (such as chlorine, bromine, and fluorine), acids, copper alloys, lead, heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arrestors. Only nonsparking tools may be used to handle cyclohexylamine. To prevent static sparks, containers and equipment should be grounded and bonded for transfers. Because containers that formerly contained cyclohexylamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyclohexylamine, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate potentially explosive atmospheres.

5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

7. For large liquid spills, build dikes far ahead of the spill to contain the cyclohexylamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 10,000 lb or more of cyclohexylamine must comply with EPA's emergency planning requirements [40 CFR Part 355.30].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for cyclohexylamine is 1 or more lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyclohexylamine emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although cyclohexylamine is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclohexylamine exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, or gauntlets, as appropriate) should be worn to prevent any skin contact with cyclohexylamine. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following materials have breakthrough times of less than 1 hr and are not recommended for use with cyclohexylamine: butyl rubber, natural rubber, neoprene, nitrile rubber, polyvinyl alcohol, polyvinyl chloride, and Viton.

If cyclohexylamine is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclohexylamine might contact the eyes (e.g., through splashes of solution). Eyewash

fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclohexylamine. Contact lenses should not be worn if the potential exists for cyclohexylamine exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYCLONITE

INTRODUCTION

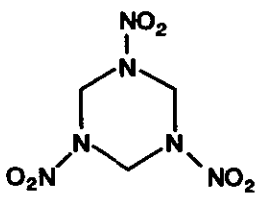
This guideline summarizes pertinent information about cyclonite for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_3H_6N_6O_6$

- **Structure**



- **Synonyms**

RDX; trimethylene trinitramine; cyclotrimethylenenitramine; cyclotrimethylenetrinitramine; hexahydro-1,3,5-trinitro-s-triazine; Hexogen 5W; Hexolite; PBX(AF) 108; sym-trimethylenetrinitramine; trinitrocyclotrimethylene triamine; 1,3,5-trinitro-1,3,5-triazacyclohexane

- **Identifiers**

1. CAS No.: 121-82-4
2. RTECS No.: XY9450000
3. DOT UN: 0072 (wetted with not <25% water, by weight, or desensitized with not <10% phlegmatizer, by weight); 0072 (wetted with not <15 percent water, by weight); 0483 (desensitized)
4. DOT label: Explosive A, corrosive

- **Appearance and odor**

Cyclonite is a white, crystalline powder that is a powerful high explosive. It is also used occasionally as a rodenticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 222.26
2. Boiling point: Data not available
3. Specific gravity (water = 1): 1.82 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 205° to 206°C (401° to 402.8°F)
6. Vapor pressure: 0.0004 mm Hg at 110°C (230°F)
7. Solubility: Insoluble in water, alcohol, benzene, car-

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

bon tetrachloride, and carbon disulfide; slightly soluble in ethyl acetate, methanol, ether, and toluene; soluble in acetone

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Shock or heat

2. Incompatibilities: Contact with mercury fulminate detonates cyclonite, and contact with combustibles or strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases (such as the oxides of nitrogen) may be released in a fire involving cyclonite.

4. Special precautions: Cyclonite is one of the most powerful explosives in use today. It must be stored in an explosives magazine and be handled accordingly.

Flammability

The National Fire Protection Association has not assigned a flammability rating to cyclonite; however, this substance is a dangerous explosion hazard.

1. Flash point: Explodes

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Evacuate the area if cyclonite or materials in the vicinity of cyclonite catch fire. This material is a high explosive and must be handled accordingly. The Fire Department should be called immediately if cyclonite is on fire or materials near this substance catch fire.

Fires involving cyclonite should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclonite.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclonite [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 1.5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 3 mg/m^3 as a short-term exposure limit (STEL), both with a "Skin" notation. A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclonite a threshold limit value (TLV) of 1.5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to cyclonite [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of central nervous system effects associated with exposure to cyclonite.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclonite can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, cyclonite is toxic to the central nervous system. The oral LD_{50}s in the rat and mouse are 100 mg/kg and 59 mg/kg, respectively; before death, these animals lost weight, became increasingly irritable, and had frequent convulsions. At autopsy, the animals showed lung and gastrointestinal tract congestion [NIOSH 1993; Clayton and Clayton 1981]. Others report an oral LD_{50} of approximately 200 mg/kg in rats [ACGIH 1991]. Seven dogs given 50 mg cyclonite/day, 6 days/week for 6 weeks showed no blood changes and did not develop methemoglobinemia; however, they became excited and irritable, had hyperactive reflexes, and convulsed and collapsed within 1 week of the onset of dosing. At autopsy, no microscopic pathology was seen [Clayton and Clayton 1981; ACGIH 1991]. The low-

est oral dose of cyclonite reported to cause developmental toxicity in the rat is 3 g/kg; 20 mg/kg cyclonite administered on days 6 to 15 of gestation caused fetotoxicity [NIOSH 1993].

2. *Effects on Humans:* In humans, cyclonite is toxic to the central nervous system. Epileptiform seizures have occurred either without warning or after a few days of insomnia, restlessness, and irritability in workers manufacturing cyclonite explosives. The seizures were most frequent in persons inhaling cyclonite-laden dust; the postconvulsive interval was characterized by temporary amnesia, malaise, fatigue, and weakness, but recovery was eventually complete [Clayton and Clayton 1981; ACGIH 1991]. Workers in a large cyclonite manufacturing plant who handled the material in the moist state did not convulse or show other signs of cyclonite poisoning, but they did develop primary irritant and sensitization dermatitis, particularly of the face and eyelids; these skin conditions are believed to have been caused by unidentified intermediates used in the manufacturing process. Patch tests confirmed that cyclonite had not caused the irritation [Clayton and Clayton 1981]. Five workers convulsed or lost consciousness after handling cyclonite in a dusty atmosphere. These workers developed headaches, nausea, vomiting, or unconsciousness either at work or later at home; unconsciousness lasted several minutes to 24 hr and was accompanied by varying degrees of stupor, nausea, vomiting, and weakness. The workers recovered completely, but two of the men became ill again when they were re-exposed to cyclonite [Clayton and Clayton 1981].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute overexposure to cyclonite include headache; irritability; fatigue; weakness; tremors; nausea; dizziness; vomiting; insomnia; unconsciousness; and seizures.

2. *Chronic exposure:* Continued low-level exposure to cyclonite can cause irritability, sleeplessness, and seizures. Cyclonite may cause skin sensitization; if sensitization occurs, very low future exposures can cause itching, the development of a skin rash, and hives.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of cyclonite. Cyclonite can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclonite or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do *not* give syrup of ipecac because of possible onset of respiratory depression and seizures.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]. All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclonite and result in worker exposures to this substance:

—Manufacture, handling, and use of cyclonite explosives, munitions, and solid propellants

—Manufacture, formulation, and application of cyclonite-containing rodenticides

The following methods are effective in controlling worker exposures to cyclonite, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cyclonite, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system and skin.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclonite at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of skin allergies or findings consistent with diseases of the central nervous system or skin.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclonite exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclonite on the central nervous system or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclonite.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyclonite is determined by using a glass fiber filter (37 mm). Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 120 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If cyclonite contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with cyclonite should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cyclonite.

A worker who handles cyclonite should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclonite or a solution containing cyclonite is handled, processed, or stored.

STORAGE

Cyclonite should be stored in a permanent explosives magazine. Detached storage is required. Containers of cyclonite should be protected from shock, friction, and physical damage and should be separated from initiator explosives, strong oxidizers, combustibles, shock, heat, sparks, and open flame. Because containers that formerly contained cyclonite may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving cyclonite, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill.
5. Use nonsparking tools for cleanup.
6. Cover the spill with soda ash and spray the area with water. Use a shovel to place the spilled material into a closed container for later disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyclonite is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cyclonite; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of cyclonite emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although cyclonite is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclonite exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cyclonite. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyclonite permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyclonite.

If cyclonite is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclonite might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclonite. Contact lenses should not be worn if the potential exists for cyclonite exposure.

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Occupational Health Guideline for Cyclopentadiene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_5H_6
- Synonyms: 1,3-Cyclopentadiene
- Appearance and odor: Colorless liquid with a sweet odor like turpentine; dimer is a crystalline material with a camphor-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyclopentadiene is 75 parts of cyclopentadiene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 200 milligrams of cyclopentadiene per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Cyclopentadiene might possibly affect the body if it is inhaled, is swallowed, or allowed to come in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to cyclopentadiene may cause irritation of the eyes and nose.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyclopentadiene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to cyclopentadiene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from cyclopentadiene exposure.

—Liver disease: Although cyclopentadiene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although cyclopentadiene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of cyclopentadiene might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Cyclopentadiene vapor is irritating to the eyes and nose and has an objectionable odor. Repeated daily exposure of rats at 500 ppm produced mild toxic effects in the liver and kidneys, whereas repeated daily exposures in several species of animals at 250 ppm for 135 times produced no manifest effects. Dogs exposed to repeated daily exposures of up to 800 ppm had no ill effects; liver function and hematologic findings remained negative. Chronic systemic effects have not been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 66
  2. Boiling point (760 mm Hg): 41.5 C (107 F)
  3. Specific gravity (water = 1): 0.8
  4. Vapor density (air = 1 at boiling point of cyclo-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

pentadiene): 2.3

5. Melting point: −85 C (−121 F)

6. Vapor pressure at 20 C (68 F): Data not available

7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Heat. Cyclopentadiene is converted to the higher boiling dicyclopentadiene on storage even at 0 C (32 F). The reaction may become violent at higher temperatures.

2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving cyclopentadiene.

4. Special precautions: Cyclopentadiene should be stored at −20 to 0 C (−4 F to 32 F). When stored in bulk, the conversion to dicyclopentadiene may become violent if the temperature is allowed to rise above 0 C (32 F).

• **Flammability**

1. Flash point: Less than 32 C (90 F) (open cup) (flash point of dimer)

2. Autoignition temperature: 640 C (1184 F)

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Dry chemical, carbon dioxide, foam

• **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, cyclopentadiene has "an irritating, terpene-like odor," but no quantitative information is available concerning its odor threshold.

The *Documentation of TLV's* states that "human sensory response was distinctly unfavorable at both 500 ppm and 250 ppm. Thus, although systemic injury is not to be expected from exposure concentrations averaging 250 ppm, a concentration significantly below 250 ppm is required from the standpoint of comfort. A TLV of 75 ppm is recommended."

2. Eye Irritation Level: Cyclopentadiene vapor is not specifically known to cause eye irritation. Grant states that "a less reactive cyclopentadiene-dimer formed by spontaneous polymerization has been tested on rabbit eyes and found to be only slightly injurious . . . ."

3. Evaluation of Warning Properties: Through its sensory effects, cyclopentadiene can be detected at a concentration of about 3 times the permissible exposure limit. For the purposes of this guideline, therefore, cyclopentadiene is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for cyclopentadiene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid cyclopentadiene.

• Clothing wet with liquid cyclopentadiene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyclopentadiene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyclopentadiene, the person performing the operation should be informed of cyclopentadiene's hazardous properties.

• Any clothing which becomes wet with liquid cyclopentadiene should be removed immediately and not reworn until the cyclopentadiene is removed from the

clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid cyclopentadiene may contact the eyes.

SANITATION

• Skin that becomes wet with liquid cyclopentadiene should be promptly washed or showered with soap or mild detergent and water to remove any cyclopentadiene.

• Employees who handle liquid cyclopentadiene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyclopentadiene may occur and control methods which may be effective in each case:

Operation	Controls
Use in thermal cracking of dicyclopentadiene; use in chemical synthesis	General dilution ventilation; personal protective equipment
Use in production of modified oil similar to tung oil from linseed or soybean oil	General dilution ventilation; personal protective equipment
Use in preparation of epoxy resins; preparation of ladder polymers; preparation of varnishes; use as a drying oil for varnishes	General dilution ventilation; personal protective equipment
Use in production of fire-resistant polyurethane foams; production of heat-stable, fire-resistant laminating agents and surface coatings; production of sanitary can coatings	General dilution ventilation; personal protective equipment
Use in production of foundry-core bindings; production of epoxidized olefins	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If cyclopentadiene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If cyclopentadiene gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If cyclopentadiene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent.

• **Breathing**

If a person breathes in large amounts of cyclopentadiene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If cyclopentadiene has been swallowed, do not induce vomiting. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If cyclopentadiene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, allow the material to dimerize, collect on paper or other material. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities may be reclaimed or dissolved in an appropriate solvent and atomized in a suitable combustion chamber. Cyclopentadiene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Cyclopentadiene may disposed of by dissolving in an appropriate solvent and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR CYCLOPENTADIENE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
750 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYCLOPENTANE

INTRODUCTION

This guideline summarizes pertinent information about cyclopentane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_5H_{10}

- **Synonyms**

  Pentamethylene

- **Identifiers**

  1. CAS No.: 287-92-3
  2. RTECS No.: GY2390000
  3. DOT UN: 1146 27
  4. DOT label: Flammable liquid

- **Appearance and odor**

  Cyclopentane is a flammable, mobile, colorless liquid with a mild, sweet odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 70.13
  2. Boiling point (760 mm Hg): 49.3°C (120.7°F)
  3. Specific gravity (water = 1): 0.75 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyclopentane): 2.42
  5. Melting point: -94°C (-137.2°F)
  6. Vapor pressure at 31°C (87.8°F): 400 mm Hg
  7. Solubility: Insoluble in water; soluble in alcohol, ether, acetone, benzene, petroleum ether, carbon tetrachloride.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame

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2. Incompatibilities: Contact of cyclopentane with strong oxidizing agents (such as chlorine, bromine, or fluorine) may cause a reaction.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide and carbon dioxide) may be released in a fire involving cyclopentane.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to cyclopentane.

1. Flash point: -37°C (-35°F) (closed cup)

2. Autoignition temperature: 361°C (682°F)

3. Flammable limits in air (% by volume): Lower, 1.1; upper, 8.7

4. Extinguishant: Use dry chemical, standard foam, or carbon dioxide to fight fires involving cyclopentane. Water may be ineffective, but it may be used to cool fire-exposed containers. If a leak or spill has not ignited, water spray may be used to disperse vapors and to protect persons attempting to stop the leak.

Fires involving cyclopentane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of cyclopentane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they heat a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyclopentane. Structural firefighters' protective clothing may provide limited protection against fires involving cyclopentane.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyclopentane [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 600 ppm (1,720 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for cyclopentane [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyclopentane a threshold limit value (TLV) of 600 ppm (1,720 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991].

- **Rationale for limits**

The NIOSH limit is based on the risk of CNS depression and skin irritation associated with cyclopentane exposure. The ACGIH limit is based on the risk of narcotic effects associated with exposure to cyclopentane.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyclopentane can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Cyclopentane is a central nervous system depressant in animals. Application of cyclopentane to the skin of guinea pigs caused redness and dryness [Clayton and Clayton 1981]. The minimal narcotic concentration in mice is 38.3 ppm; this level of exposure may also cause loss of reflexes and death. The margin of safety between the minimal narcotic dose and the lethal dose is thus very small [Clayton and Clayton 1981]. Exposure to a cyclopentane concentration of 112 to 1,139 ppm for 6 hours/day for 3 weeks caused no effects in male and

female rats; however, exposure to 8,110 ppm for 6 hours/day for 12 weeks caused a decrease in the rate of body weight gain in female rats [Clayton and Clayton 1981].

2. *Effects on Humans:* Cyclopentane is a central nervous system depressant in humans. Because the industrial use of pure cyclopentane is limited and the commercial reagents and solvents that contain cyclopentane also contain other hydrocarbons, there are few toxicologic data on the effects of exposure to the pure substance [ACGIH 1991]. Prolonged contact of this substance with the skin may produce dryness and cracking [NJDH 1989]. Exposure to a 10 to 15 ppm concentration of cyclopentane for an unspecified period is reported to have been tolerated by volunteers [Clayton and Clayton 1981]. The central nervous system effects of exposure to cyclopentane include lightheadedness, dizziness, excitement, incoordination, nausea, vomiting, loss of consciousness, and, if exposure is severe, death due to respiratory failure [Sittig 1985]. One hundred twenty-two Italian shoc factory workers exposed for unspecified periods to unidentified concentrations of glue solvents that contained both cyclopentane and n-hexane developed polyneuropathy; however, the extent to which these polyneuropathies were attributable to cyclopentane exposure is unclear [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to cyclopentane may include lightheadedness, dizziness, excitement, incoordination, nausea, vomiting, stupor, loss of consciousness, and death. Contact with cyclopentane can irritate the skin and eyes.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to cyclopentane include dryness and cracking of the skin. Although cyclopentane has not been adequately evaluated for the possibility of brain and nerve damage following repeated exposures, other solvents and petroleum-based chemicals have been shown to cause such damage, including: reduced memory and concentration, fatigue, sleep disturbances, and reduced coordination.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of cyclopentane. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if cyclopentane or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve cyclopentane and lead to worker exposures to this substance:

—Use in cracking of aromatics

—Use as an intermediate in the production of various chemicals and pharmaceuticals, including analgesics, sedatives, hypnotics, antitumor agents, prostaglandins, depressants, and insecticides

—Use as a component of solvents used for cellulose ethers, motor fuels, and as an azeotropic distillation agent

—Use in the production of cyclopentadiene

—Use as a laboratory chemical

The following methods are effective in controlling worker exposures to cyclopentane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to cyclopentane, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system.

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to cyclopentane at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to cyclopentane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of cyclopentane on the skin and central nervous system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for cyclopentane.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne cyclopentane is made using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 5 liters is collected. The sample is then treated with carbon disulfide to extract the cyclopentane. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If cyclopentane contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with cyclopentane should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of cyclopentane.

A worker who handles cyclopentane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where cyclopentane or a solution containing cyclopentane is handled, processed, or stored.

STORAGE

Cyclopentane should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must meet OSHA requirements for Class IB flammable liquids. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of cyclopentane should be protected from physical damage and should be stored separately from strong oxidizing agents (such as chlorine, bromine, and fluorine), heat, sparks, and open flame. Drums must be equipped with self-closing valves, pressure vacuum bungs, and flame arresters. Only nonsparking tools may be used to handle cyclopentane. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained cyclopentane may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving cyclopentane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the cyclopentane for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Cyclopentane is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of cyclopentane; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of cyclopentane emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although cyclopentane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of cyclopentane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowl-

edgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with cyclopentane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. Butyl rubber and natural rubber have been tested against permeation by cyclopentane and have breakthrough times of less than one hour; therefore, they are not recommended for use with cyclopentane. No other reports were found on the resistance of additional protective clothing materials to cyclopentane permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyclopentane.

If cyclopentane is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which cyclopentane might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyclopentane. Contact lenses should not be worn if the potential exists for cyclopentane exposure.

REFERENCES CITED

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Occupational Health Guideline for 2,4-D *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Cl_2C_6H_3OCH_2COOH$
- Synonyms: 2,4-Dichlorophenoxyacetic acid
- Appearance and odor: Colorless, odorless solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2,4-D is 10 milligrams of 2,4-D per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2,4-D can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Massive exposure to 2,4-D may cause weakness, stupor, muscle twitching, and convulsions. Contact of the material with the skin may cause a rash. It has caused minor liver and kidney damage in animals.

2. Long-term Exposure: Not known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 2,4-D.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2,4-D at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 2,4-D exposure.

—Liver disease: 2,4-D causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: 2,4-D causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Cardiovascular disease: 2,4-D causes ventricular fibrillation in animals. In persons with impaired cardiovascular function, the inhalation of 2,4-D might cause exacerbation of pre-existing disorder.

—Skin disease: 2,4-D can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Convulsive disorder or neuropathy: 2,4-D may cause convulsions in humans. Persons with a history of such disorders may be more susceptible to the effects of this agent. 2,4-D may also produce neuropathy by analogy to effects observed in experimental animals.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

2,4-D dust causes signs of both hypo- and hyperexcitation of the central nervous system in animals. In several species of animals given massive oral doses, sudden death has been ascribed to ventricular fibrillation. If death is delayed, myotonia, stiffness of the extremities, ataxia, paralysis, and coma are seen; autopsy findings have included minor liver and kidney injury. The myotonia characteristic of intoxication by 2,4-D in animals has not been reported in humans. Possibly the only recognized fatal case of poisoning involved a suicidal person who ingested not less than 6500 mg; the

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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person apparently experienced violent convulsions, although they were not actually observed; there were no significant findings at autopsy. A single dose of 3.6 g of 2,4-D administered intravenously to a patient for treatment of disseminated coccidiomycosis caused stupor, hyporeflexia, fibrillary twitching of some muscles, and urinary incontinence; 24 hours after the dose, the patient still complained of profound muscular weakness, which subsided after an additional 24 hours. Contact of the material with the skin may cause dermatitis; skin absorption is slight.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 221
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.1 (estimated)
4. Vapor density (air = 1 at boiling point of 2,4-D): 7.63
5. Melting point: 140 C (284 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, at 20 C (68 F): 0.07 ppm
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving 2,4-D.
4. Special precautions: None

- **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical, foam, water

- **Warning properties**

Since 2,4-D has a negligible vapor pressure, warning properties are not considered.

Grant states that "2,4-dichlorophenoxyacetic acid (2,4-D) is a herbicide for weed control, often used in the form of its salts or esters. Parenteral administration to dogs has caused sneezing, lacrimation, and rubbing of the eyes, along with gastrointestinal disturbances. In three human beings, absorption of an unspecified ester of dichlorophenoxyacetic acid through the skin caused polyneuritis, but with no disturbance of the eyes or vision." The above do not appear to be local effects on the eye. However, Stolman and Stecher note that this substance can cause irritation of the eyes.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for 2,4-D is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with 2,4-D or liquids containing 2,4-D.
- If employees' clothing may have become contaminated with 2,4-D, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with 2,4-D should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2,4-D from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 2,4-D, the person performing the operation should be informed of 2,4-D's hazardous properties.
- Non-impervious clothing which becomes contami-

nated with 2,4-D should be removed promptly and not reworn until the 2,4-D is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where 2,4-D or liquids containing 2,4-D may contact the eyes.

SANITATION

• Skin that becomes contaminated with 2,4-D should be promptly washed or showered with soap or mild detergent and water to remove any 2,4-D.

• Eating and smoking should not be permitted in areas where solid 2,4-D is handled, processed, or stored.

• Employees who handle 2,4-D or liquids containing 2,4-D should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2,4-D may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of herbicides	Process enclosure; local exhaust ventilation; personal protective equipment; washing facilities
Manufacture of 2,4-D	Process enclosure; local exhaust ventilation; personal protective equipment; washing facilities
Application on cereal crops, corn, sorghum, milo, sugar cane, pastures, range land, and lawns for use as an herbicide; use as a plant hormone on agricultural crops	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If 2,4-D or liquids containing 2,4-D get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If 2,4-D or liquids containing 2,4-D get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 2,4-D or liquids containing 2,4-D penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of 2,4-D, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When 2,4-D has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If 2,4-D is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dispose of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device, as in below or deposit in a secured sanitary landfill.

• Waste disposal methods:

2,4-D may be disposed of:

1. By making packages of 2,4-D in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving 2,4-D in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By disposal in a secured sanitary landfill.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 15, 1977.

RESPIRATORY PROTECTION FOR 2,4-D

Condition	Minimum Respiratory Protection* Required Above 10 mg/m³
Particulate Concentration	
100 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
500 mg/m³ or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s), and dust filter(s), including pesticide respirators which meet the requirements of this class. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter, including pesticide respirators which meet the requirements of this class. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DDT

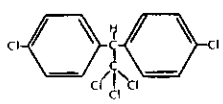
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about DDT for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_{14}H_9Cl_5$
- **Structure:**



- **Synonyms:** Citox; genitox; dichlorodiphenyltrichloroethane; 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane
- **Identifiers:** CAS 50-29-3; RTECS KJ3325000; DOT 2761
- **Appearance and odor:** Colorless crystals or white to slightly off-white powder with a slightly aromatic odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 354.48
2. Boiling point (at 760 mmHg): 260°C (500°F)
3. Specific gravity (water = 1): 1.56
4. Vapor density (air = 1 at boiling point of DDT): 12.2
5. Melting point: 105-109°C (221-228°F)
6. Vapor pressure at 20°C (68°F): 1.5 x 10^{-7} mmHg
7. Practically insoluble in water

- **Reactivity**

1. Incompatibilities: DDT should not be stored in iron containers; DDT should not be mixed with iron and aluminum salts or with alkaline materials. Temperatures greater than 100°C (212°F) may cause decomposition.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride) may be released in a fire involving DDT.
3. Caution: DDT should be stored in a tightly closed container in a well-ventilated area.

- **Warning properties**

Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for DDT is 1 milligram of DDT per cubic meter of air (mg/m³) as a time-weighted average (TWA) concentration over an 8-hour workshift (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that DDT be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.5 mg/m³ as a TWA for up to a 10-hour workshift, 40-hour workweek. The NIOSH REL is the lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 1 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek; the short-term exposure limit (STEL) is 3 mg/m³ (Table 1).

Table 1.—Occupational exposure limits for DDT

	Exposure limits mg/m³
OSHA PEL TWA (Skin)*	1
NIOSH REL TWA (CA)†	0.5§
ACGIH TLV® TWA	1

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ Lowest reliably detectable level.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

NOTE: A general ban was ordered by the Environmental Protection Agency on the registration of DDT, effective December 31, 1972. Effective the same date, the ban for uses of DDT by public health officials in disease control programs and by USDA and the military for health quarantine and prescription drugs use was lifted.

HEALTH HAZARD INFORMATION

• Routes of exposure

DDT may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

Effects on animals: Acute oral administration of DDT to rats caused tissue destruction (necrosis) of the liver, mild degeneration of kidney tubules, and changes in electroencephalograms. Chronic oral administration of DDT caused decreased fertility in rats and increased mortality of their offspring, toxic effects on the liver (including necrosis, fat deposition, increased weight, and increased enzyme activity), and liver cancer. In mice, chronic oral administration of DDT produced cancers of the liver, lungs, and lymphatic system.

• Signs and symptoms of exposure

Short-term (acute): Exposure to DDT can cause a prickling sensation of the tongue, lips, and face, a general feeling of ill health, headache, fatigue, vomiting, dizziness, tremors, convulsions, partial paralysis of the hands, and coma. DDT can also cause irritation of the eyes and skin.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to DDT, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic or laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, and reproductive and nervous systems.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DDT at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include chronic liver disease. Workers should inform their physicians of their potential for exposures to DDT because internal absorption of this chemical pathologically increases the liver's ability to metabolize and eliminate medications which may be prescribed or taken "over the counter."

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DDT. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, and reproductive and nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to DDT may cause adverse reproductive effects or diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to DDT should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting DDT vapors with charcoal adsorption tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure DDT may also be used if available. A detailed sampling and analytical method for DDT may be found in the *NIOSH Manual of Analytical Methods* (method number S 274).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with DDT.

SANITATION

Clothing which is contaminated with DDT should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of DDT from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DDT's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with DDT should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DDT should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to DDT may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for DDT

Operations	Controls
During preparation and handling of insecticide	Process enclosure, local exhaust ventilation, personal protective equipment
During maintenance of equipment and storage containers	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to DDT, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DDT gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to DDT, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DDT gets on the skin, wash it immediately with soap and water. If DDT penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DDT is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities of liquids containing DDT, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing DDT may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. If in solid form, DDT may be collected and placed in an appropriate container.
5. DDT dust may be collected by vacuuming with an appropriate high-efficiency filtration system.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or

minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for DDT

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DECABORANE

INTRODUCTION

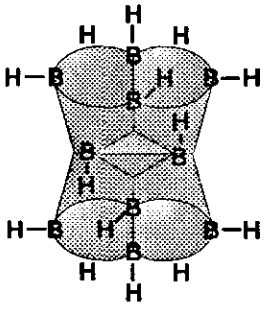
This guideline summarizes pertinent information about decaborane for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $B_{10}H_{14}$

- **Structure**



- **Synonyms**

  Decaboron tetradecahydride, boron hydride

- **Identifiers**

  1. CAS No.: 17702-41-9
  2. RTECS No.: HD1400000
  3. DOT UN: 1868 34
  4. DOT label: Flammable solid, poison

- **Appearance and odor**

  Decaborane is a colorless to white crystalline solid with a bitter, chocolate-like odor. The median odor threshold for decaborane is 0.06 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 122.3
  2. Boiling point (760 mm Hg): 213°C (416°F)
  3. Specific gravity (water = 1): 0.94 at 25°C (77°F)
  4. Vapor density (air = 1 at boiling point of decaborane): 4.2
  5. Melting point: 99.7°C (211°F)
  6. Vapor pressure at 25°C (77°F): 0.05 mm Hg
  7. Solubility: Slightly soluble in cold water; soluble in

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benzene, hexane, toluene, alcohol, and ether; very soluble in carbon disulfide

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of decaborane with oxidizers, oxygenated solvents, or dimethyl sulfoxide causes fires or explosions. In contact with carbon tetrachloride, ethers, or halocarbons, decaborane forms impact-sensitive mixtures.

3. Hazardous decomposition products: Toxic fumes (such as boron oxides) may be released in a fire involving decaborane.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to decaborane.

1. Flash point: 80°C (176°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, waterspray, or regular foam to fight fires involving decaborane.

Fires involving decaborane should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of decaborane may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving decaborane. Structural firefighters' protective clothing may provide limited protection against fires involving decaborane.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for decaborane is 0.05 ppm (0.3 mg/m^3) as an 8-hr time-weighted average (TWA) concentration. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.3 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek and a STEL of 0.15 (0.9 mg/m^3). A STEL is the maximum 15-min concentration to which workers may be exposed during any 15-min period of the working day. The NIOSH REL and STEL also bear a "Skin" notation [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned decaborane a threshold limit value (TLV) of 0.05 ppm as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 0.15 ppm for periods not to exceed 15 minutes. The ACGIH also assigns decaborane a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The OSHA, NIOSH, and ACGIH limits are based on the risk of neuropathic, hepatic, and nephrotoxic effects associated with exposure to decaborane [54 Fed. Reg. 2409; NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to decaborane can occur through inhalation, ingestion, eye and skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Decaborane is toxic to the central nervous system, liver, cardiovascular system, and kidneys of experimental animals. It is toxic by all routes of exposure, and cumulative effects have been reported in rats, rabbits, and dogs [Clayton and Clayton 1981; Parmeggiani 1983]. Corneal opacities developed in mice and rats following a 4-hr exposure to a 26-ppm concentration of decaborane [Hathaway et al. 1991]. The dermal LD_{50} is 71 mg/kg in rabbits and 740 mg/kg in rats [NIOSH 1993]. The 4-hr LC_{50} is 46 ppm in rats and 12 ppm in mice [NIOSH 1993]. The oral LD_{50} is 64 mg/kg in rats and 41 mg/kg in mice [NIOSH 1993]. The manifestations of acute decaborane-induced central nervous system toxicity in rodents include hyperexcitability, restlessness, coarse head movements, generalized weakness, rigid hindquarters, absent eye reflexes, convulsive seizures, depressed breathing, and narcosis [Parmeggiani 1983; Hathaway et al. 1991]. Repeated low-dose oral exposure (3 mg/kg) to decaborane did not cause marked central nervous system effects in any test species but did cause liver and kidney damage [Hathaway et al. 1991]. Cardiovascular toxicity is manifested in dogs as slow heart rate, initial moderate elevation in blood pressure, and a final drop in blood pressure after lethal doses of decaborane are administered by any route [Hathaway et al. 1991; Parmeggiani 1983].

2. *Effects on Humans:* Decaborane causes central nervous system effects in humans. Exposure causes headaches, dizziness, drowsiness, and nausea, and severe exposure is expected to cause general weakness, incoordination, hyperexcitability, narcosis, fatigue, muscle spasms, tremors, convulsions, and unconsciousness [Hathaway et al. 1991]. The onset of symptoms may be delayed for up to 2 days. Recovery from muscle spasms may occur in 24 hours, but lightheadedness and fatigue may be present for up to 3 days [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to decaborane may include headache, dizziness, drowsiness, nausea, lightheadedness, fatigue, and incoordination. Based on effects seen in animals, exposure may cause redness and irritation of the eyes and eyelids, tremor, localized muscle spasm, and convulsions.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to decaborane may include headaches, fatigue, drowsiness, inability to concentrate, and lack of coordination. Based on effects seen in animals, chronic exposure may lead to jaundice, enlarged and tender liver, and blood, pus, or protein in the urine.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure*: If particulates, mists, or vapors of decaborane are inhaled, move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if decaborane or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions muse be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve decaborane and lead to worker exposures to this substance:

—Use as a reducing agent in chemical synthesis and as an olefin polymerization catalyst

—Use as a vulcanizing agent in rubber manufacture and as an anti-corrosive coating for metals

—Manufacture of high-energy fuel, rocket propellants, plastics, and polymers

—Use as a stabilizer, rayon delustrant, mothproofing agent, dye-stripping agent, fluxing agent, and oxygen scavenger

The following methods are effective in controlling worker exposures to decaborane, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to decaborane, a licensed health care profes-

sional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the central nervous system, liver, kidneys, eyes, and skin.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to decaborane at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the central nervous system, liver, kidneys, eyes, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to decaborane exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of decaborane on the central nervous system, liver, kidneys, eyes, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Borate concentrations can be measured in the serum of exposed individuals, and some sources state that serum borate concentrations greater than 20 mg/liter indicate excessive exposure. However, no biological monitoring test acceptable for routine use has yet been developed for decaborane because serum borate levels do not correlate well with airborne concentrations.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne decaborane is made using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 480 liters is collected. Analysis is conducted by inductively coupled plasma/atomic emission spectrometry. The limit of detection for this procedure is not known. Analysis is performed for total boron and then back-calculated for decaborane. This method is described in the OSHA Laboratory In-House File [OSHA 1991].

PERSONAL HYGIENE

If decaborane contacts the skin, workers should flush the affected areas immediately with 3 percent aqueous ammonia hydroxide, followed by washing with soap and water.

Clothing contaminated with decaborane should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of decaborane, particularly its potential to cause burns of the skin.

A worker who handles decaborane should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, applying cosmetics, or using toilet facilities.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where decaborane or a solution containing decaborane is handled, processed, or stored.

STORAGE

Decaborane should be stored in a cool, dry, well-ventilated area in tightly sealed, weather-proof containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of decaborane should be protected from physical damage and should be stored separately from oxidizers, oxygenated solvents, dimethyl sulfoxide, heat, sparks, and open flame. Only nonsparking tools may be used to handle decaborane. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained decaborane may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving decaborane, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
6. For large liquid spills, build dikes far ahead of the spill to contain the decaborane for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Employers owning or operating a facility at which there are 10,000 lb or more of decaborane must comply with EPA's emergency planning requirements. (If decaborane is in the form of a finely divided powder or is handled in solution or in molten form, the employer must comply with these requirements if 500 lb or more of decaborane are present at the facility.)

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

  The reportable quantity for decaborane is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hour period in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of any State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of decaborane emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although decaborane is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], the EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of decaborane exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent any skin contact with decaborane. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to decaborane permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to decaborane.

If decaborane is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which decaborane might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with decaborane. Contact lenses should not be worn if the potential exists for decaborane exposure.

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Occupational Health Guideline for Demeton

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5O)_2PSOC_2H_4SC_2H_5$
- Synonyms: Systox(R); O-O-diethyl O-(2-ethylthio)-ethyl phosphorothioate (2 parts) Demeton-O; O-O-diethyl S-(2-ethylthio)ethyl phosphorothioate (1 part) Demeton-S
- Appearance and odor: Light brown liquid with the odor of sulfur compounds

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Demeton is 0.1 milligram of Demeton per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for Demeton a Threshold Limit Value of 0.01 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Demeton can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of Demeton, breathing and eye effects are the first to appear. These include tightness of the chest, wheezing, a bluish discoloration of the skin, small pupils, aching in and behind the eyes, blurring of vision, tearing, runny nose, headache, and watering of the mouth. After swallowing Demeton, loss of appetite, nausea, vomiting, abdominal cramps and diarrhea may appear within two hours. After skin absorption, sweating and twitching in the area of absorption may occur usually within 15 minutes to four hours. With severe intoxication by all routes, in addition to all the above symptoms, weakness, generalized twitching, and paralysis may occur and breathing may stop. In addition, dizziness, confusion, staggering, slurred speech, generalized sweating, irregular or slow heart beat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to Demeton may make a person more susceptible to the effects of this and related chemicals. Repeated exposures to concentrations which are too small to produce symptoms after a single exposure may result in the onset of symptoms.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to Demeton.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Demeton at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of reduced pulmonary function, convulsive disorders, or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, nervous system, cardiovascular system and attention to the cholinesterase levels in the blood should be stressed. The skin should be examined for evidence of chronic disorder.

—Cholinesterase determination: Demeton (Systox) causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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in the serum and erythrocytes should be determined by using medically acceptable biochemical tests prior to any new period of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception of the cholinesterase determination which should be performed quarterly or at any time overexposure is suspected or signs or symptoms of toxicity occur.

- **Summary of toxicology**

Demeton (Systox) is an anticholinesterase agent; absorption may occur from inhalation of the vapor, by skin absorption, or by ingestion of the liquid. At least four fatal, several severe nonfatal, and a number of mild cases of Demeton intoxication have been reported. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nervous system, skeletal and smooth muscle, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms may occur promptly or may be delayed for up to 12 hours. After inhalation, respiratory and ocular effects are the first to appear, often within a few minutes after exposure. Respiratory effects include tightness in the chest and wheezing due to bronchoconstriction and excessive bronchial secretion; laryngeal spasms and excessive salivation may add to the respiratory distress; cyanosis may also occur. Ocular effects include miosis, aching in and behind the eyes (attributed to ciliary spasm), blurring of distant vision, tearing, rhinorrhea, and frontal headache. After ingestion, gastrointestinal effects, such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption, localized sweating and muscular fasciculations in the immediate area occur, usually within 15 minutes to 4 hours; skin absorption is somewhat greater at higher ambient temperatures and is increased by the presence of dermatitis. With severe intoxication by all routes, an excess of acetylcholine at the neuromuscular junctions of skeletal muscle causes weakness aggravated by exertion, involuntary twitchings, fasciculations, and eventually paralysis; the most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. The blood pressure may fall to low levels, and cardiac irregularities including complete heart block may occur; these effects may sometimes be reversed by establishing adequate pulmonary ventilation. Complete symptomatic recovery usually occurs within 1 week; increased susceptibility to the effects of anticholinesterase agents persists for weeks after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 258
  2. Boiling point (2 mm Hg): 134 C (273 F)
  3. Specific gravity (water = 1): 1.18
  4. Vapor density (air = 1 at boiling point of Demeton): Not applicable
  5. Melting point: Higher than −25 C (−13 F)
  6. Vapor pressure at 20 C (68 F): Very low
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, phosphoric acid mist, and carbon monoxide) may be released when Demeton decomposes.
  4. Special precautions: Demeton will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Data not available
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**
  1. Odor Threshold: No quantitative information is available concerning the odor threshold of Demeton.
  2. Eye Irritation Level: Demeton is not known to be an eye irritant.
  3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of Demeton, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for Demeton is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with Demeton.

• Clothing which has had any possibility of being contaminated with Demeton should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of Demeton from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the Demeton, the person performing the operation should be informed of Demeton's hazardous properties.

• Where there is any possibility of exposure of an employee's body to Demeton, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with Demeton should be removed immediately and not reworn until the Demeton is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of Demeton contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to Demeton, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with Demeton should be immediately washed or showered with soap or mild detergent and water to remove any Demeton.

• Workers subject to skin contact with Demeton should wash any areas of the body which may have contacted Demeton at the end of each work day.

• Eating and smoking should not be permitted in areas where Demeton is handled, processed, or stored.

• Employees who handle Demeton should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Demeton may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of acaricides and insecticides	Personal protective equipment
Application as a pesticide on agricultural crops, fruits/nuts, vegetables, and ornamentals	Material substitution; personal protective equipment
Manufacture of Demeton	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If Demeton or Demeton mists get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If Demeton or Demeton mists get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If Demeton or Demeton mists penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of Demeton, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When Demeton has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If Demeton is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.

2. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

Demeton may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

2. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DEMETON (R)

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Vapor Concentration	
1 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 20 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of Demeton; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 20 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIACETONE ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about diacetone alcohol for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_6H_{12}O_2$
- **Structure:** $(CH_3)_2C(OH)CH_2COCH_3$
- **Synonyms:** Diketone alcohol; 4-hydroxy-2-keto-4-methylpentane; 4-hydroxy-4-methyl-2-pentanone; 2-methyl-2-pentanol-4-one
- **Identifiers:** CAS 123-42-2; RTECS SA9100000; DOT 1148, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless to yellow liquid with a mild odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.62
2. Boiling point (at 760 mmHg): 169.2 °C (335 °F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of diacetone alcohol): 4.0
5. Melting point: -43 °C (-45 °F)
6. Vapor pressure: At 20 °C (68 °F), 0.8 mmHg; at 25 °C (77 °F), 1.2 mmHg
7. Miscible in water
8. Evaporation rate (butyl acetate = 1): 0.14
9. Saturation concentration in air (approximate) at 20 °C (68 °F): 0.10% (1,000 ppm); at 25 °C (77 °F), 0.16% (1,600 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong alkalies may cause formation of flammable acetone vapors.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving diacetone alcohol.
3. Caution: Diacetone alcohol will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 57.8 °C (136 °F) (closed cup)
2. Autoignition temperature: 643 °C (1,190 °F)
3. Flammable limits in air, % by volume: Lower, 1.8; upper, 6.9
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class II Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.28 ppm
2. Eye irritation level: 100 ppm
3. Other information: Nasal irritation may occur at 100 ppm.
4. Evaluation of warning properties for respirator selection: Because of its odor, diacetone alcohol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, it is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for diacetone alcohol is 50 parts of diacetone alcohol per million parts of air (ppm) [240 milligrams of diacetone alcohol per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 50 ppm (240 mg/m³) as a TWA for up to a 10-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 50 ppm (240 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for diacetone alcohol

	Exposure limits ppm	mg/m³
OSHA PEL TWA	50	240
NIOSH REL TWA	50	240
ACGIH TLV® TWA	50	240

HEALTH HAZARD INFORMATION

• **Routes of exposure**
Diacetone alcohol may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**
Effects on animals: In rats and rabbits, acute oral administration or inhalation of diacetone alcohol caused narcosis, kidney damage, and liver damage (vacuolization and granulation of parenchymal cells).

• **Signs and symptoms of exposure**
1. *Short-term (acute):* Exposure to diacetone alcohol can cause chest discomfort, narcosis, and irritation of the eyes, nose, and throat.
2. *Long-term (chronic):* Exposure to diacetone alcohol can cause dryness, irritation, and inflammation of the skin.

RECOMMENDED MEDICAL PRACTICES

• **Medical surveillance program**
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• **Preplacement medical evaluation**
Prior to placing a worker in a job with a potential for exposure to diacetone alcohol, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, and nervous and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to diacetone alcohol at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include concurrent dermatitis or a history of chronic skin disease.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to diacetone alcohol. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, liver, kidneys, and nervous and respiratory systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination**
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population.

• **Sentinel health events**
Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**
Measurements to determine worker exposure to diacetone alcohol should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of

consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

Sampling and analysis may be performed by collecting diacetone alcohol vapors with charcoal tubes followed by desorption with 2-proponal in carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure diacetone alcohol may also be used if available. A detailed sampling and analytical method for diacetone alcohol may be found in the *NIOSH Manual of Analytical Methods* (Method number 1402).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with diacetone alcohol.

Workers should be provided with and required to use splash-proof goggles where diacetone alcohol may come in contact with the eyes.

SANITATION

Clothing which is contaminated with diacetone alcohol should be removed immediately and placed in closed containers for storage until it can be discarded or until provision is made for the removal of diacetone alcohol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of diacetone alcohol's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with diacetone alcohol should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle diacetone alcohol should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to diacetone alcohol may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for diacetone alcohol

Operations	Controls
During application of nitrocellulose lacquer	Process enclosure, local exhaust ventilation, personal protective equipment
During application of paper and textile coatings, wood stains, and preservatives; during use and manufacture of artificial silk and leather, quick-drying inks, photographic film, antifreeze preparations, and hydraulic fluids	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a solvent for cellulose esters, epoxy resins, hydrocarbons, oils, fats, resin gums, dyes, tars, cements, and waxes; during use as a pigment solvent in the dyeing industry	Local exhaust ventilation, general dilution ventilation, personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to diacetone alcohol, an eye-wash fountain should be provided within the immediate work area for emergency use.

If diacetone alcohol gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to diacetone alcohol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If diacetone alcohol gets on the skin, wash it immediately with soap and water. If diacetone alcohol penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If diacetone alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing diacetone alcohol, absorb on paper towels and place in an appropriate container. Place towels in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from diacetone alcohol vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing diacetone alcohol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Diacetone alcohol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing diacetone alcohol may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection, only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 3.—Respiratory protection for diacetone alcohol

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
	Any powered air-purifying respirator with organic vapor cartridge(s) (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 1,250 ppm	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 2,100 ppm	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 2,100 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 50 ppm (240 mg/m^3) (TWA).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIAZINON

INTRODUCTION

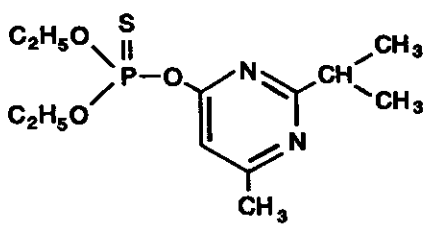
This guideline summarizes pertinent information about diazinon for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

$C_{12}H_{21}N_2O_3PS$

- **Structure**



- **Synonyms**

Diazinone; isopropylmethylpyrimidyl diethyl thiophosphate; Alfa-tox; Basudin; Flytrol; Garden Tox; Knox-out; Nipsan; Oleod-iazinon; O,O-diethyl O-(2-isopropyl-4-methyl-6-pyrimidyl)thionophosphate.

- **Identifiers**

1. CAS No.: 333-41-5
2. RTECS No.: TF3325000
3. DOT NA: 2783 55
4. DOT label: None

- **Appearance and odor**

Pure diazinon is a colorless liquid; however, the technical grade of diazinon has a faint odor and is pale yellow to dark brown in color. Diazinon is an organophosphate pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 304.4
2. Boiling point (0.002 mm Hg): 83° to 84°C (181° to 183°F)
3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): 0.00041 mm Hg

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility: Slightly soluble in water; soluble in organic solvents; miscible with petroleum ether, alcohol, cyclohexane, ether, and benzenes.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Water, heat, sparks, and open flame.

2. Incompatibilities: Contact of diazinon with water, copper-containing compounds, oxidizers, acids, or bases may cause a violent reaction.

3. Hazardous decomposition products: Toxic particulates and gases (such as oxides of nitrogen, phosphorus, sulfur, and carbon monoxide) may be released in a fire involving diazinon.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a fire hazard rating to diazinon.

1. Flash point: 180°F (82.2°C)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving diazinon should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of diazinon may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diazinon. Chemical protective clothing specifically recommended for diazinon may not provide thermal protection unless so stated by the manufacturer. Structural firefighters' protective clothing may not provide protection against permeation by diazinon.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diazinon [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has eatablished a recommended exposure limit (REL) of 0.1 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diazinon a threshold limit value (TLV) of 0.1 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek. The ACGIH also assigns a "Skin" notation to diazinon [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and skin irritation and cholinesterase inhibition associated with diazinon exposure. The ACGIH limit is based on the risk of cholinesterase inhibition associated with exposure to diazinon.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diazinon can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Diazinon is classified as a moderately toxic organophosphate pesticide [EPA 1989]; it is a cholinesterase inhibitor in experimental animals. Applied to the skin of rabbits under open conditions, 500 mg of diazinon caused moderate systemic toxicity but no primary irritation [NIOSH 1993]. The dermal LD_{50} in rabbits is 180 mg/kg

[NIOSH 1993]. The oral LD_{50} in rats is 66 mg/kg, and the LC_{50} in the same species is 3500 mg/m^3 for 4 hours [NIOSH 1993]. In one study, rats fed diazinon at a dose of 50 mg/kg/day for 72 weeks showed complete inhibition of red blood cell cholinesterase activity and marked inhibition of brain cholinesterase activity but no other signs of toxicity [ACGIH 1991]. In another study, rats fed 10, 100, or 1,000 ppm diazinon in the diet for 72 weeks showed no adverse effects [Clayton and Clayton 1981]. Dogs fed diazinon at a dose of 9.3 mg/kg/day promptly lost weight and showed signs of poisoning and developed tremor; at a dose of 4.6 mg/kg/day for 12 weeks, reversible cholinesterase activity was seen in these animals [Hayes 1982]. Rhesus monkeys tolerated diazinon in the diet at a dose of 0.05 mg/kg/day for 2 years without effect; inhibition of both plasma and red blood cell cholinesterase was moderate or erratic when the dose was increased to 0.5 mg/kg/day, and marked decreases in cholinesterase activity occurred at 5 mg/kg/day [Hayes 1982].

2. *Effects on Humans:* Diazinon is an organophosphate pesticide of moderate toxicity [EPA 1989]; it is a cholinesterase inhibitor in humans. In contact with the skin, diazinon may cause allergic skin reactions; this substance has also caused fatalities when absorbed through the skin [NLM 1992]. In a series of tests involving 2 to 4 volunteers, oral diazinon doses of 0.05 mg/kg/day for 28 days caused a 35- to 40-percent reduction in cholinesterase activity in plasma but had no effect on red blood cell cholinesterase activity [ACGIH 1991]. Diazinon administered at an oral dose of 0.02 mg/kg/day for 37 days caused a 14-percent reduction in plasma cholinesterase activity, an amount difficult to distinguish from normal variation [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to diazinon may cause cholinesterase inhibition. The signs and symptoms of cholinesterase inhibition include headache, dizziness, anxiety, restlessness, confusion, bizarre behavior, muscle twitching, weakness, tremor, incoordination, nausea, vomiting, diarrhea, abdominal cramps, sweating, salivation, tearing, blurred vision, constricted pupils, chest tightness, wheezing, cough, rales, bradycardia or tachycardia, and hypertension.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to low doses of cholinesterase inhibitors include, in addition to those listed above, anorexia, weakness, and malaise.

- **Emergency Procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result from exposure to particulates or concentrated solutions, vapors, mists, or aerosols of diazinon. diazinon can be absorbed through the skin in lethal amounts! ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* If particulates or vapors, mists, or aerosols of diazinon are inhaled, move the victim to fresh air ***immediately***. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if diazinon or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve diazinon and may result in worker exposures to this substance:

—Use as a soil insecticide and lawn and garden spray

—Use for insect control on fruits, vegetables, tobacco, forage, field crops, and ornamentals

—Manufacture and formulation of diazinon-containing pesticides

—Use as a pet spray

The following methods are effective in controlling worker exposures to diazinon, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for exposure to diazinon, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the cholinesterase activity level of the blood (plasma and red blood cells).

  A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to diazinon at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with reductions in plasma or red blood cell cholinesterase activity. To establish a baseline, plasma and red blood cell cholinesterase activity readings should be taken

before the worker is exposed to organophosphate pesticides.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diazinon on plasma or red blood cell cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of plasma or red blood cell cholinesterase activity is a nonspecific, qualitative indicator of exposure to organophosphorus chemicals such as diazinon. Red blood cell cholinesterase activity can be an indicator either of acute overexposure or of cumulative chronic exposure to diazinon. A red blood cell cholinesterase level that is equal to 70 percent of the worker's preexposure baseline level is recommended by some sources as a biological exposure index for organophosphates.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne diazinon is determined using an OSHA Versatile Sampler (OVS-2), 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh), with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.09 and is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

Diazinon can be absorbed through the skin in toxic amounts. Therefore, if diazinon contacts the skin, workers should repeatedly and vigorously wash the affected areas immediately with soap and water.

Clothing contaminated with diazinon should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles diazinon should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where diazinon or a solution containing diazinon is handled, processed, or stored.

STORAGE

Diazinon should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of diazinon should be protected from physical damage and should be stored separately from water, oxidizers, acids or bases, heat, sparks, and open flame. Because containers that formerly contained diazinon may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diazinon, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. Water spray may be used to reduce vapors.

6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

8. For large liquid spills, build dikes far ahead of the spill to contain the diazinon for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Diazinon is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal authorities.

  The reportable quantity for diazinon is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hour period, in a manner that will expose persons outside the facility, employers are required to do the following:

  —Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

  —Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

  —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diazinon emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although diazinon is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace

concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of diazinon exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with diazinon. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to diazinon permeation. However, permeation tests with similar compounds (other organophosphorus compounds) have shown that a laminate of Viton/neoprene or butyl rubber/neoprene provides good protection against permeation by this group of substances. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to diazinon.

If diazinon is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which diazinon might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with diazinon.

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Occupational Health Guideline for Diazomethane *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2N_2
- Synonyms: Azimethylene; diazirine
- Appearance: Yellow gas. When stored under pressure, diazomethane can be in the liquid form.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diazomethane is 0.2 part of diazomethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of diazomethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diazomethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to diazomethane vapor may cause severe irritation of the eyes, nose, throat, skin, and lungs. Symptoms include headache, weakness, cough, fever, chest pains, shortness of breath, and wheezing. The onset of symptoms after exposure may be delayed. Skin and mucous membrane exposure to liquids containing diazomethane may cause burns with the loss of the skin or mucous membrane. If any of these symptoms appear, get medical attention immediately.

2. Long-term Exposure: Prolonged or repeated exposure to diazomethane may lead to sensitization. Should sensitization occur, a person may experience asthma-like symptoms or fever from exposure to concentrations of diazomethane which had previously caused no symptoms. Diazomethane has been reported to cause cancer of the lungs in animals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diazomethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diazomethane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of respiratory system should be stressed.

—14" x 17" chest roentgenogram: Diazomethane may cause acute lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Diazomethane is reported to cause temporary pulmonary function impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Diazomethane gas is a severe respiratory irritant and sensitizer. It is one of the most dangerous products of the chemical laboratory, causing irritation of the eyes, chest pain, cough, fever, and severe asthmatic attacks. Exposure of cats to 175 ppm for 10 minutes resulted in pulmonary edema and hemorrhage, with death occurring in 3 days. A chemist briefly exposed to an unknown concentration in a laboratory developed a violent cough and shortness of breath leading to severe pul-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

monary edema; symptoms completely subsided within 2 weeks. In a fatal incident, another chemist exposed to an unknown concentration of diazomethane, as well as other irritant gases, experienced immediate respiratory distress leading to pneumonitis and death on the fourth day after exposure. A physician exposed to diazomethane from a laboratory spill noted only a faint odor, but immediately experienced severe headache, cough, mild anterior chest pain, generalized aching of muscles, and a sensation of overwhelming tiredness. Within 5 minutes he was stuporous, and on early admission to hospital was markedly flushed and feverish; he recovered in approximately 48 hours. Subsequent exposure to trace amounts of the gas produced wheezing, cough, and malaise, leading to the suspicion that this substance may have a sensitizing, as well as an irritating, effect upon the respiratory system. Skin irritation and sensitization occurs. Also mutagenic and carcinogenic effects have been reported in animals.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 42
2. Boiling point (760 mm Hg): −23 C (−9 F)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of diazomethane): 1.4
5. Melting point: −145 C (-229 F)
6. Vapor pressure at 20 C (68 F): Not pertinent
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not pertinent

- **Reactivity**

1. Conditions contributing to instability: Diazomethane may explode when not diluted with other inert gases such as nitrogen. Exposure of diazomethane gas or solutions in solvents to sunlight or other bright illumination may cause explosions. Contact with rough edges such as ground glass may cause explosions.
2. Incompatibilities: Contact of diazomethane gas with alkali metals or drying agents such as calcium sulfate will cause explosions.
3. Hazardous decomposition products: Data not available
4. Special precautions: Barriers or shields should be utilized to protect employees from accidental explosions.

- **Flammability**

1. Flash point: Not pertinent
2. Autoignition temperature: Pure material explodes above 150 C (302 F). Impure material explodes at lower temperature.
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Stop flow of gas.

- **Warning properties**

1. Odor Threshold: Patty reports that diazomethane has a musty odor. No quantitative data are available, however, relating the odor to air concentrations.
2. Eye Irritation Level: Grant reports that "irritation of the eye from exposure to the gas has developed occasionally among those working with this substance." The concentrations causing eye irritation are not given.
3. Other Information: Patty reports that diazomethane is a severe respiratory tract irritant, but the concentrations producing this irritation are not given.
4. Evaluation of Warning Properties: Patty reports that "the warning properties of diazomethane are not adequate to prevent serious intoxication or fatalities." Based upon this report and upon the lack of quantitative data relating warning properties to air concentrations of diazomethane, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube containing XAD-2 resin coated with octanoic acid, followed by desorption with carbon disulfide and gas chromatographic analysis. An analytical method for diazomethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming contaminated with liquid diazomethane or solutions containing diazomethane or from becoming frozen from contact with vessels containing liquid diazomethane.

• Clothing wet with flammable solutions containing diazomethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diazomethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diazomethane, the person performing the operation should be informed of diazomethane's hazardous properties.

• Any clothing which becomes wet with liquid diazomethane or flammable solutions containing diazomethane should be removed immediately and not reworn until the flammable liquids are removed from the clothing.

• Non-impervious clothing which becomes contaminated with solutions containing diazomethane should be removed promptly and not reworn until the diazomethane is removed from the clothing.

• Employees should be provided with and required to use safety goggles where there is any possibility of liquid diazomethane or solutions containing diazomethane contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid diazomethane or solutions containing diazomethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with solutions containing diazomethane should be promptly washed or showered with soap or mild detergent and water to remove any solutions.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diazomethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as methylating agent in chemical analysis and laboratory organic synthesis	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid diazomethane or solutions containing diazomethane get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid diazomethane or solutions containing diazomethane get on the skin, immediately flush the contaminated skin with water. If liquid diazomethane or solutions containing diazomethane soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of diazomethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If diazomethane has been swallowed, do not induce vomiting. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If diazomethane is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, allow to vaporize.

• Waste disposal method:

Diazomethane may be disposed of by burning at a safe location or in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 7, 1974.

RESPIRATORY PROTECTION FOR DIAZOMETHANE

Condition	Minimum Respiratory Protection* Required Above 0.2 ppm
Gas Concentration	
2 ppm or less**	Any supplied-air respirator. Any self-contained breathing apparatus.
10 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Diborane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: B_2H_6
- Synonyms: Boroethane
- Appearance and odor: Colorless gas with a repulsive, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diborane is 0.1 part of diborane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.1 milligram of diborane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diborane can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Diborane may cause tightness in the chest, cough, inability to take a deep breath, and chest pain. Severe breathing difficulties may occur. These difficulties may be delayed in onset. High concentrations of diborane may irritate the eyes.

2. Long-term Exposure: Prolonged exposure to low concentrations of diborane may cause headache, lightheadedness, fatigue, muscular weakness, and tremors. It has caused liver and kidney damage in animals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diborane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diborane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the lungs, nervous system, liver, and kidneys should be stressed.

—14" x 17" chest roentgenogram: Diborane causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Diborane is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

- **Summary of toxicology**

Diborane gas is a pulmonary irritant. The LC50 for rats was 50 ppm for 4 hours; in other animal experiments, acute exposure caused pulmonary edema and hemorrhage and temporary damage to the liver and kidneys. In humans, overexposure results in a sensation of tightness in the chest leading to precordial pain, shortness of breath, nonproductive cough, and sometimes nausea. Prolonged exposure to low concentrations causes headache, light-headedness, vertigo, chills and, less frequently, fever; fatigue or weakness occurs and may persist for several hours; tremor or muscular fasciculations occur infrequently and are usually localized and of short duration. Diborane gas has not been found to have significant effects upon contact with skin or mucous

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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membranes, although high concentrations may cause eye irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 27.7
2. Boiling point (760 mm Hg): −92 C (−134 F)
3. Specific gravity (water = 1): 0.47 (liquid)
4. Vapor density (air = 1 at boiling point of diborane): 0.96
5. Melting point: −165 C (−265 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts rapidly to form hydrogen gas
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above −18 C (0 F). Containers are usually stored in "dry ice." Ignites spontaneously in moist air at room temperature.
2. Incompatibilities: Contact with air or halogenated compounds will cause fires and explosions. Contact with aluminum, lithium, and other active metals forms hydrides which may ignite spontaneously. Diborane reacts with many oxidized surfaces as a strong reducing agent.
3. Hazardous decomposition products: Toxic gases and vapors (such as boron oxide smoke) may be released in a fire involving diborane.
4. Special precautions: Diborane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: 38 − 52 C (100 − 125 F)
3. Flammable limits in air, % by volume: Lower: 0.8; Upper: 98
4. Extinguishant: Stop flow of gas, or let fire burn.

- **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, the nauseating odor of diborane is "not a reliable warning of toxic exposure." No quantitative information is available concerning the threshold of odor, however.
2. Eye Irritation Level: Diborane is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of diborane, it is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

At the time of publication of this guideline, no measurement method for diborane had been published by NIOSH.

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diborane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a reducing agent in the synthesis of organic chemical intermediates; use as a component or additive for high-energy fuels; use as a catalyst in olefin polymerization	Process enclosure; personal protective equipment
Use in electronics industry to improve crystal growth or to impart electrical properties in pure crystals	Process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If strong concentrations of diborane gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Breathing**

If a person breathes in large amounts of diborane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If diborane is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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RESPIRATORY PROTECTION FOR DIBORANE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
1 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against diborane. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

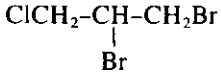
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIBROMOCHLOROPROPANE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about dibromochloropropane (DBCP) for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** $C_3H_5Br_2Cl$
- **Structure:**



- **Synonyms:** 1-Chloro-2,3-dibromopropane; DBCP; 1,2-dibromo-3-chloropropane
- **Identifiers:** CAS 96-12-8; RTECS TX8750000; DOT 2872, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Dense yellow or amber liquid or granular solid with a pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 236.35
2. Boiling point (at 760 mmHg): 195°C (383°F)
3. Specific gravity (water = 1): 2.093
4. Melting point: 6°C (43°F)
5. Vapor pressure at 20°C (68°F): 0.8 mmHg
6. Solubility in water, g/100 g water at 20°C (68°F): 0.1
7. Saturation concentration in air (approximate) at 20°C (68°F): 0.1% (1000 ppm)

- **Reactivity**

1. Incompatibilities: DBCP reacts with chemically active metals such as aluminum, magnesium, and tin alloys.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen bromide, hydrogen chloride, and carbon monoxide) may be released in a fire involving DBCP.
3. Caution: DBCP will attack some rubber materials and coatings.

- **Flammability**

1. Flash point: 77°C (170°F) (open cup)
2. Extinguishant: Carbon dioxide or dry chemical
3. Class IIIA Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

1. Odor threshold: 0.01-0.03 ppm
2. Evaluation of warning properties for respirator selection: Because of the lack of odor at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), DBCP is treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The Occupational Safety and Health Administration (OSHA) considers DBCP to be a cancer hazard. The current OSHA permissible exposure limit (PEL) for DBCP is 1 part of DBCP per billion parts of air (ppb) as a time-weighted average (TWA) concentration over an 8-hour workshift; the employer shall assure that no employee is exposed to eye or skin contact with DBCP. The NIOSH REL is 10 ppb as a TWA [0.1 milligrams of DBCP per cubic meter of air (mg/m^3)] for up to a 10-hour workshift, 40-hour workweek; however, the NIOSH REL has been superseded by the OSHA standard promulgated in 1978. The American Conference of Governmental Industrial Hygienists (ACGIH) does not have an assigned threshold limit value (TLV®) for DBCP.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

DBCP may cause adverse health effects following exposure via inhalation or dermal or eye contact.

- **Summary of toxicology**

1. *Effects on animals:* In rats, acute inhalation or oral administration of DBCP caused central nervous system depression with sluggishness and loss of muscular coordination (ataxia), weight loss, and decreased spermatogenesis; acute dermal exposure caused dermal and subcutaneous tissue destruction (necrosis).

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Subchronic inhalation of DBCP by rats, guinea pigs, rabbits, or monkeys produced necrosis of the liver, kidney, spleen, testes, or seminiferous tubules; reduction in sperm count; abnormal sperm; or inhibition of the estrous cycle. Cancers of the nasal cavity, tongue, pharynx, lungs, stomach, adrenal glands, or mammary glands have been reported for rats or mice chronically exposed to DBCP by inhalation or oral administration.

2. *Effects on humans:* Low-level repeated or prolonged exposure of male workers has been associated with low sperm count, chromosome abnormality, sterility, decreased testicular size, and increased level of follicle stimulating hormone. These effects have not been associated with exposure in previous years, indicating that they may be reversible following removal from exposure.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to DBCP can cause drowsiness, nausea, vomiting, and irritation of the eyes, nose, throat and skin.

2. *Long-term (chronic):* Exposure to DBCP can cause congestion or fluid in the lungs and inflammation of the eyes or skin.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to DBCP, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys, urinary tract, and reproductive and respiratory systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to DBCP at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

• Periodic medical screening and/or biologic monitoring

Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to DBCP. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function and integrity of the eyes, skin, liver, kidneys, urinary tract, and respiratory and reproductive systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and tests of lung function.

• Medical practices recommended at the time of job transfer or termination

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to DBCP may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• Sentinel health events

1. Acute SHE's include: Contact and/or allergic dermatitis.
2. Delayed-onset or reproductive SHE's include: Infertility in exposed males.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to DBCP should be taken so that the TWA exposure is based on a single entire

workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Method**

There are no NIOSH validated sampling and analytical methods for DBCP.

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, face shields (8-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with DBCP.

Workers should be provided with and required to use dust- and splash-proof safety goggles where DBCP or other dust may come in contact with the eyes.

SANITATION

Clothing which is contaminated with DBCP should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of DBCP from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DBCP's hazardous properties.

Change and shower rooms should be provided with separate locker facilities for street and work clothes.

Skin that becomes contaminated with DBCP should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle DBCP should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to DBCP may occur and control methods which may be effective in each case are listed in Table 1.

Table 1.—Operations and methods of control for dibromochloropropane

Operations	Controls
During the manufacture of DBCP	Completely enclosed processes, local exhaust ventilation, personal protective equipment
During the formulation of DBCP into pesticides and fumigants	Local exhaust ventilation, protective clothing and equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to DBCP, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DBCP gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to DBCP, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DBCP gets on the skin, wash it immediately with soap and water. If DBCP penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If DBCP is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing DBCP, absorb on paper towels and place in an appropriate container. Place towels

in a safe place such as a fume hood for evaporation. Allow sufficient time for evaporation of the vapors so that the hood ductwork is free from DBCP vapors. Burn the paper in a suitable location away from combustible materials.

4. Large quantities of liquids containing DBCP may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. DBCP should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

5. DBCP liquid or solid may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations, including those requiring confined-space entry (Table 2).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

For each level of respiratory protection only those respirators that have the minimum required protection factor and meet other use restrictions are listed. All respirators that have higher protection factors may also be used.

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Table 2.—Respiratory protection for dibromochloropropane

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister having a high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-n-DIBUTYLAMINOETHANOL

INTRODUCTION

This guideline summarizes pertinent information about 2-n-dibutylaminoethanol for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_{10}H_{23}NO$

- **Structure**

  $(C_4H_9)_2NCH_2CH_2OH$

- **Synonyms**

  2-Dibutylaminoethanol; N,N-di-n-butylaminoethanol; beta-n-dibutylaminoethyl alcohol; N,N-dibutylethanolamine; N-N-dibutyl-n-(2-hydroxyethyl)amine; DBAE

- **Identifiers**

  1. CAS No.: 102-81-8
  2. RTECS No.: KK3850000
  3. DOT UN: 2873 55
  4. DOT label: St. Andrew's Cross

- **Appearance and odor**

  2-n-Dibutylaminoethanol is a combustible, colorless liquid with a faint, amine-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 173.3
  2. Boiling point (760 mm Hg): 224° to 232°C (435° to 450°F)
  3. Specific gravity (water = 1): 0.86 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of 2-n-dibutylaminoethanol): 6.0
  5. Melting point: Data not available
  6. Vapor pressure at 20°C (68°F): 0.1 mm Hg
  7. Solubility: Slightly soluble in water; soluble in methanol, ethyl ether, acetone, gasoline, benzene, and ethyl acetate.

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8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of 2-n-dibutylaminoethanol with oxidizing materials causes a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide and oxides of nitrogen) may be released in a fire involving 2-n-dibutylaminoethanol.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 2 (moderate fire hazard) to 2-n-dibutylaminoethanol.

1. Flash point: 93°C (200°F) (closed cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or foam to fight fires involving 2-n-dibutylaminoethanol.

Fires involving 2-n-dibutylaminoethanol should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of 2-n-dibutylaminoethanol may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2-n-dibutylaminoethanol. Chemical protective clothing that is specifically recommended for 2-n-dibutylaminoethanol may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving 2-n-dibutylaminoethanol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 2-n-dibutylaminoethanol [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 2 ppm (14 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2-n-dibutylaminoethanol a threshold limit value (TLV) of 2 ppm (14 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 2-n-dibutylaminoethanol [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on acetylcholinesterase inhibition in vitro and weight loss in animals associated with 2-n-dibutylaminoethanol [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2-n-dibutylaminoethanol can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* 2-n-Dibutylaminoethanol causes irritation of the eyes and skin on acute exposure and liver and kidney damage on longer exposure. In contact with the skin of rabbits, 2-n-dibutylaminoethanol caused severe irritation [NIOSH 1993]. Application of 0.005 ml undiluted 2-n-dibutylaminoethanol to the

eyes of rabbits caused severe corneal injury [Grant 1986]. The oral LD_{50} in rats is 1,070 mg/kg, and the dermal LD_{50} in rabbits is 1,680 mg/kg [NIOSH 1993]. One of 5 rats exposed to a 70-ppm concentration of 2-n-dibutylaminoethanol for 6 hours/day, 5 days/week for 1 week died; in addition, compared with controls, exposed rats had a 57-percent average body weight loss, a 2-fold increase in liver- and kidney-to-body weight ratios, a 10-fold increase in serum bilirubin, a slightly elevated clotting time, and an elevated hematocrit. Exposure to a 22-ppm concentration of 2-n-dibutylaminoethanol on the same regimen for 27 weeks produced no changes in exposed rats [ACGIH 1991]. Rats fed 2-n-dibutylaminoethanol for 5 weeks at doses greater than 0.13 g/kg/day had elevated kidney-to-body weight ratios at autopsy, although no histologic changes were evident [ACGIH 1991].

2. *Effects on Humans:* Exposure to 2-n-dibutylaminoethanol causes irritation of the eyes, nose, throat, and skin in humans [NJDH 1987]. By analogy with the effects caused by chemically similar compounds, exposure to 2-n-dibutylaminoethanol may also cause allergic reactions, such as asthma or skin rashes [NJDH 1987]. In vitro studies show that 2-n-dibutylaminoethanol inhibits the enzyme acetylcholinesterase [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 2-n-dibutylaminoethanol include redness and inflammation of the eyes and eyelids, runny nose, scratchy throat, redness and inflammation of the skin, and acetylcholinesterase inhibition. Symptoms of acetylcholinesterase inhibition include headache, sweating, nausea, vomiting, diarrhea, muscle twitching, coma, and death.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to 2-n-dibutylaminoethanol may include abdominal tenderness, enlarged liver, jaundice, and pus or blood in the urine.

- **Emergency procedures**

> **WARNING!**
>
> **Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of 2-n-dibutylaminoethanol. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if 2-n-dibutylaminoethanol or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

   —Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operation may involve 2-n-dibutyl-

aminoethanol and lead to worker exposure to this substance:

—Organic synthesis

The following methods are effective in controlling worker exposures to 2-n-dibutylaminoethanol, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to 2-n-dibutylaminoethanol, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, respiratory system, and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to 2-n-dibutylaminoethanol at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with allergies or with diseases of the liver, kidneys, respiratory system, or skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to 2-n-dibutylaminoethanol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2-n-dibutylaminoethanol on the liver, kidneys, respiratory system, or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for 2-n-dibutylaminoethanol.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne 2-n-dibutylaminoethanol is made using a silica gel tube (300/150 mg sections, 45/60 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 24 liters is collected. Immediately after sampling, each section of the tube should be transferred to a separate vial containing 2 milliliters of desorbing solution (0.12 M HCl in 4:1 methanol:water). Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1992] and in Method No. 2007 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If 2-n-dibutylaminoethanol contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with 2-n-dibutylaminoethanol should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the irritant properties of 2-n-dibutylaminoethanol.

A worker who handles 2-n-dibutylaminoethanol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where 2-n-dibutylaminoethanol is handled, processed, or stored.

STORAGE

2-n-Dibutylaminoethanol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of 2-n-dibutylaminoethanol should be protected from physical damage and should be stored separately from oxidizers (such as perchlorates, peroxides, and permanganates), heat, sparks, and open flame. To prevent static sparks, all equipment used in the manufacturing, use, or storage of this substance should be grounded and bonded. Because containers that formerly contained 2-n-dibutylaminoethanol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2-n-dibutylaminoethanol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use water spray to reduce vapors.
6. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the 2-n-dibutylaminoethanol for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of

hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

2-n-Dibutylaminoethanol is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of 2-n-dibutylaminoethanol; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of 2-n-dibutylaminoethanol emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although 2-n-dibutylaminoethanol is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of 2-n-dibutylaminoethanol exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets, as necessary) should be worn to prevent prolonged or repeated skin contact with 2-n-dibutylaminoethanol. Chemical protective clothing should be selected on the

basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to 2-n-dibutylaminoethanol permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to 2-n-dibutylaminoethanol.

If 2-n-dibutylaminoethanol is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which 2-n-dibutylaminoethanol might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with 2-n-dibutylaminoethanol. Contact lenses should not be worn when working around this material.

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Occupational Health Guideline for Dibutyl Phosphate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_4H_9O)_2(OH)PO$
- Synonyms: Dibutyl acid o-phosphate; di-n-butyl hydrogen phosphate; dibutyl phosphoric acid
- Appearance and odor: Colorless to brown odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dibutyl phosphate is 1 part of dibutyl phosphate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of dibutyl phosphate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dibutyl phosphate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Dibutyl phosphate may cause irritation of the eyes, nose, throat, and lungs. It may also cause headaches.

2. Long-term Exposure: Repeated or prolonged exposure to dibutyl phosphate may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dibutyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dibutyl phosphate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from dibutyl phosphate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of dibutyl phosphate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Dibutyl phosphate can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Dibutyl phosphate vapor is a respiratory irritant. In rats the oral LD50 is 3.2 g/kg. Data on effects in humans are sparse; workers exposed to unspecified concentrations of vapor complained of respiratory irritation and headache. It is a moderately strong acid and could be expected to be irritating on contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 210
2. Boiling point (760 mm Hg): Higher than 100 C (212 F) (decomposes)
3. Specific gravity (water = 1): 1.06
4. Vapor density (air = 1 at boiling point of dibutyl phosphate): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Much less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F):

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None hazardous

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume and carbon monoxide) may be released in a fire involving dibutyl phosphate.

4. Special precautions: Liquid dibutyl phosphate will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Carbon dioxide, dry chemical, foam

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of dibutyl phosphate.

2. Eye Irritation Level: Dibutyl phosphate vapor is not known to be an eye irritant.

3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of dibutyl phosphate, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for dibutyl phosphate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid dibutyl phosphate, where skin contact may occur.

• Clothing wet with liquid dibutyl phosphate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dibutyl phosphate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dibutyl phosphate, the person performing the operation should be informed of dibutyl phosphate's hazardous properties.

• Where exposure of an employee's body to liquid dibutyl phosphate may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with dibutyl phosphate should be removed promptly and not reworn until the dibutyl phosphate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid dibutyl phosphate may contact the eyes.

SANITATION

• Skin that becomes contaminated with dibutyl phosphate should be promptly washed or showered with soap or mild detergent and water to remove any dibutyl phosphate.

• Employees who handle liquid dibutyl phosphate should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dibutyl phosphate may occur and

control methods which may be effective in each case:

Operation	Controls
Use as a catalyst in manufacture of phenolic and urea resins	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in metal separation and extraction	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid dibutyl phosphate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid dibutyl phosphate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid dibutyl phosphate soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of dibutyl phosphate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When liquid dibutyl phosphate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If liquid dibutyl phosphate is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Dibutyl phosphate may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Dibutyl Phosphate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• Hawley, G. G. (ed.): *The Condensed Chemical Dictionary* (8th ed. rev.), Van Nostrand Reinhold, New York, 1971.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR DIBUTYL PHOSPHATE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
10 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
125 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 125 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Dibutylphthalate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_4(CO_2C_4H_9)_2$
- Synonyms: DBP; dibutyl 1,2-benzenedicarboxylate
- Appearance and odor: Colorless, oily liquid with a very weak, aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dibutylphthalate is 5 milligrams of dibutylphthalate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dibutylphthalate can affect the body if it is swallowed, comes in contact with the eyes or skin, or is inhaled as a mist or spray.

- **Effects of overexposure**

Swallowing dibutylphthalate may cause nausea, dizziness, light sensitivity, and watering and redness of the eyes. Overexposure to hot vapors or mists of dibutylphthalate may cause nose and throat irritation.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to dibutylphthalate.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to dibutylphthalate at potentially hazardous levels.

- **Summary of toxicology**

Extensive experience with dibutylphthalate as an insect repellant has shown that it is relatively non-irritating to the skin, eyes, and mucous membranes. Aerosols from heated dibutylphthalate may cause irritation of the eyes and upper respiratory tract. In one report of a human case, accidental ingestion of ten grams of this compound by a chemical operator produced nausea and dizziness with lacrimation, photophobia, and conjunctivitis, but recovery was prompt and uneventful. Animal experiments to determine dermal and oral toxicity of dibutylphthalate showed that extremely high doses were considered necessary to produce toxic effects. Dibutylphthalate was found to be teratogenic by intraperitoneal injection of doses representing 1/10, 1/8, and 1/3 of the LD50 value into female rats at the 5th, 10th, and 15th day of gestation. This probably is of no significance in industrial exposures.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 278
  2. Boiling point (760 mm Hg): 335 C (635 F)
  3. Specific gravity (water = 1): 1.05
  4. Vapor density (air = 1 at boiling point of dibutylphthalate): 9.6
  5. Melting point: −37 C (−35 F)
  6. Vapor pressure at 20 C (68 F): Less than 0.01 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.45
  8. Evaporation rate (butyl acetate = 1): Almost zero
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, and strong acids may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving dibutylphthalate.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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4. Special precautions: None

- **Flammability**

1. Flash point: 157 C (315 F) (closed cup)
2. Autoignition temperature: 403 C (757 F)
3. Flammable limits in air, % by volume: Lower: 0.5 (calculated at flash point)
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

According to Grant, "contact with the surface of human eyes has occurred by accidental droplet splash as well as by experimental application, and this has caused immediate, severe, stinging pain. The pain stimulated profuse tearing, which washed the oily liquid away, and the eyes were not appreciably damaged."

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of dibutylphthalate on a filter, followed by extraction with carbon disulfide, and gas chromatographic analysis. An analytical method for dibutylphthalate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use splash-proof safety goggles where liquid dibutylphthalate may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dibutylphthalate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray application of polyvinyl acetate surface coatings by spraying, dipping, or crushing	Local exhaust ventilation; personal protective equipment
Liberation during spray application of polyester and epoxy resins	Local exhaust ventilation; personal protective equipment
Liberation during hand and dip applications of polyvinyl acetate, and polyester and epoxy resins	General dilution ventilation
Liberation during molding and forming of cellulose acetate butyrate, acetate, propionate, and polyvinyl acetate	Local exhaust ventilation; personal protective equipment
Liberation during application of polyvinyl acetate adhesives, both solvent and hot-melt types	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of nitrile rubber; during molding of polyester and epoxy articles	General dilution ventilation
Liberation during manufacture of polyvinyl acetate surface coatings	General dilution ventilation
Use during spray application of nitrocellulose lacquer surface coatings, including paper coatings	Local exhaust ventilation

Operation	Controls
Liberation during forming of ethyl cellulose articles; during production of polyvinyl acetate; during production of cellulose acetate butyrate, cellulose acetate propionate, and polyvinyl acetate adhesives	General dilution ventilation
Liberation during brush application of nitrocellulose surface coatings; during manufacture of polyester and epoxy resins; during manufacture of nitrocellulose surface coatings	General dilution ventilation
Liberation during manufacture of explosives and propellants	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If dibutylphthalate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention if any discomfort continues. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If dibutylphthalate saturates the clothing, remove and clean the clothing before wearing it again. Wash any dibutylphthalate from the skin regularly, particularly when there has been much skin contact. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of dibutylphthalate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When dibutylphthalate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing respiratory protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If dibutylphthalate is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber.

• Waste disposal methods:

Dibutylphthalate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Dibutylphthalate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• Karel, L., et al.: "The Intraperitoneal Toxicity of Some Glycols, Glycol Ethers, Glycol Esters, and Phthalates in Mice," *Journal of Pharmacology and Experimental Therapeutics,* 90:338-347, 1947.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Singh, A. R., et al.: "Teratogenicity of Phthalate Esters in Rats," *Journal of Pharmaceutical Sciences,* 61:51-55, 1972.

• Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Dibutylphthalate,* New York, 1971.

RESPIRATORY PROTECTION FOR DIBUTYLPHTHALATE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
250 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
9300 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 9300 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICHLOROACETYLENE

INTRODUCTION

This guideline summarizes pertinent information about dichloroacetylene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  C_2Cl_2

- **Structure**

  ClC ≡ CCl

- **Synonyms**

  Dichloroethyne; 1,2-dichloroacetylene

- **Identifiers**

  1. CAS No.: 7572-29-4
  2. RTECS No.: AP1080000
  3. DOT UN: May not be transported.
  4. DOT label: Forbidden

- **Appearance and odor**

  Dichloroacetylene is a combustible, volatile, self-reactive liquid with an isocyanide-like odor. This material is not produced or used commercially; it is an undesirable byproduct of the dehydrochlorination or incomplete incineration of trichloroethylene.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 94.9
  2. Boiling point (760 mm Hg): Explodes on boiling at 32° to 33°C (90° to 91°F)
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: -66° to -64.2°C (-86.8° to -83.6°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water; soluble in alcohol, ethanol, and acetone
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: shock, heat, sparks, open flame, acids, oxidizing materials, or contact with the air.

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2. Incompatibilities: Contact of dichloroacetylene with air causes autoxidation and may cause an explosion; contact with acids or oxidizing materials also may cause a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide, phosgene, and chlorine) may be released in a fire involving dichloroacetylene.

4. Special precautions: Dichloroacetylene explodes or ignites on contact with air and explodes if it reaches boiling temperature. Also, in air, unstabilized dichloroacetylene decomposes to phosgene, chloroform, carbon tetrachloride, trichloroacryloyl chloride, and hexachlorobutadiene.

Flammability

The National Fire Protection Association has not assigned a fire hazard rating to dichloroacetylene. However, this substance is known to be spontaneously combustible and to pose a severe explosion hazard when exposed to heat or shock.

1. Flash point: Spontaneously combustible

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use carbon dioxide, water spray, or regular foam. Do not use any chemical extinguishants because dichloroacetylene is shock-sensitive and contact with the surface of dry chemicals may increase its explosive potential. Do not use more water than is necessary to extinguish the fire because it will scatter the fire.

Fires involving dichloroacetylene should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dichloroacetylene because poisonous gases (such as phosgene and hydrogen chloride) may be produced in a fire.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dichloroacetylene [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.4 mg/m^3) as a ceiling limit. A worker's exposure to dichloroacetylene shall at no time exceed this ceiling level [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dichloroacetylene a ceiling limit value of 0.1 ppm (0.9 mg/m^3), which should not be exceeded during any part of the working day [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer, neurotoxicity, and CNS depression and also the formation of kidney tumors in animals associated with dichloroacetylene exposure. The ACGIH limit is based on the risk of nausea and other systemic effects associated with exposure to dichloroacetylene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dichloroacetylene can occur through inhalation and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Dichloroacetylene causes kidney and liver damage and cancer in experimental animals. In mice, a 1-hr LC_{50} of 124 ppm and a 4-hr LC_{50} of 19 ppm have been reported. The cause of death was kidney injury [Clayton and Clayton 1981]. A 6-hr LC_{50} in mice of 19 ppm has also been reported [RTECS 1991]. Exposure to dichloroacetylene concentrations of 126, 202, or 307 ppm for 1 hour or to 17 to 23 ppm for 6 hours caused neuropathological changes, kidney and liver damage, and death among rabbits [Clayton and Clayton 1981; IARC 1986]. Rats exposed continuously to a 2.8-ppm concentration of dichloroacetylene for 90 days became emaciated and showed hind limb weakness and kidney injury, and one animal became blind [Grant 1986]. Rats exposed for 6 hours/day, 5 days/week for 6

weeks to a 9.8-ppm concentration of dichloroacetylene (along with 50-ppm trichloroacetylene) or to 15.5 ppm dichloroacetylene (along with 150 ppm trichloroacetylene) were unkempt in appearance and showed signs of respiratory distress; rats in the 15.5-ppm group also showed marked kidney injury at autopsy [Clayton and Clayton 1981]. Dichloroacetylene has been tested for carcinogenicity in inhalation bioassays in mice and rats. Male mice showed dose-related increases in the incidence of adenocarcinomas of the kidney, and rats of both sexes showed an increased incidence of lymphomas and also developed benign tumors of the liver and kidney [IARC 1986]. Based on these data, the International Agency for Research on Cancer has concluded that there is limited evidence that dichloroacetylene is carcinogenic in animals [IARC 1986].

2. *Effects on Humans:* In humans, dichloroacetylene causes eye irritation, headache, nausea, and vomiting as well as nervous system injury and death. As a neurotoxin, dichloroacetylene has an affinity for the cranial nerves [IARC 1986]. Exposure to a 0.5- to 1-ppm concentration of dichloroacetylene for prolonged (not further specified) periods caused nausea in 85 percent of exposed individuals [ACGIH 1991]. Members of a submarine crew developed loss of appetite, nausea that progressed to vomiting, itching around the eyes, headache, sore gums, intense pain in the upper jaw, and facial and oral herpes 3 to 4 days after exposure to dichloroacetylene [IARC 1986]. Tank car cleaners developed fatigue, headache, nausea, and vomiting; these workers also experienced a loss of sensation in the trigeminal nerve distribution that persisted for periods ranging from several days to years [IARC 1986]. Thirteen cases of dichloroacetylene-induced cranial nerve palsy and nine cases of herpes were reported in the 1940s. One patient died 3 days after exposure and a second died 13 days later; autopsy revealed cerebral edema in both of these cases [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dichloroacetylene include redness, inflammation, and itching of the eyes and eyelids, weakness of the eye muscles, headache, nausea, vomiting, sore gums, painful jaws, loss of sensation in the lips and mucous membranes, fatigue, and facial and oral herpes characterized by painful blisters around the mouth.

2. *Chronic exposure:* Based on effects seen in animals, chronic exposure to dichloroacetylene may cause liver or kidney damage, with jaundice, enlarged and tender liver, and pus, protein, or blood in the urine.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dichloroacetylene. ***Immediately and thoroughly*** flush eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dichloroacetylene or any material containing it is ingested:

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

   —Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may evolve dichloroacetylene and lead to worker exposures to this substance:

—Thermal dehydrochlorination of trichloroethylene

—Degradation of trichloroethylene, vinylidene chloride, or other hydrocarbons by pyrolysis at temperatures above 70°C (158°F), photolysis, or contact with alkaline materials

—Exposure of trichloroethylene vapors to Hopcalite in a closed environment or to soda lime in closed-circuit anesthesia machines

—Exposure of trichloroethylene liquid to a caustic substance in degreaser tanks

The following methods are effective in controlling worker exposures to dichloroacetylene, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

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MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to dichloroacetylene, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the liver, kidneys, and sensory nerves.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dichloroacetylene at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of

exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the liver, kidneys, or sensory nerves.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dichloroacetylene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dichloroacetylene on the liver, kidneys, or sensory nerves. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dichloroacetylene.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne dichloroacetylene is determined using a solid sorbent (charcoal) tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 1 liter is collected. The sample is then treated with carbon disulfide to extract the dichloroacetylene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

If dichloroacetylene contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with dichloroacetylene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dichloroacetylene.

A worker who handles dichloroacetylene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dichloroacetylene is handled, processed, or stored.

STORAGE

Dichloroacetylene should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Storage areas must be equipped with explosion-proof electrical equipment and fittings. Containers of dichloroacetylene should be protected from physical damage and should be stored separately from strong acids, oxidizers, potassium, sodium, aluminum powder, heat, sparks, and open flame. Only nonsparking tools may be used to handle dichloroacetylene. An automatic pump should be used to transfer liquid dichloroacetylene from drums or storage containers to process containers. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dichloroacetylene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dichloroacetylene, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup

has been completed. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Isolate the area of the spill or leak.
3. Remove all sources of heat and ignition.
4. If possible to do so without risk, attempt to stop the leak.
5. Ventilate the area of the spill or leak.
6. For small liquid spills, absorb with earth, sand, vermiculite, or other absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes to contain the spill.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Dichloroacetylene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dichloroacetylene; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dichloroacetylene emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dichloroacetylene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dichloroacetylene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1901.134]. Such a program must include respi-

rator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves, boots, aprons, and gauntlets should be worn as necessary to prevent prolonged or repeated skin contact with dichloroacetylene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dichloroacetylene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dichloroacetylene.

If dichloroacetylene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dichloroacetylene might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with dichloroacetylene. Contact lenses should not be worn when the potential for exposure to dichloroacetylene exists.

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Occupational Health Guideline for o-Dichlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: 1,2-$C_6H_4Cl_2$
- Synonyms: 1,2-Dichlorobenzene; o-dichlorobenzol
- Appearance and odor: Colorless to pale yellow liquid with a pleasant aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for o-dichlorobenzene is a ceiling of 50 parts of o-dichlorobenzene per million parts of air (ppm). This may also be expressed as 300 milligrams of o-dichlorobenzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

o-Dichlorobenzene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may also be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: o-Dichlorobenzene vapor may cause irritation of the upper respiratory tract and eyes. Higher concentrations may cause drowsiness, unconsciousness, and death. The liquid may cause burning of the skin. The liquid may also cause burning of the eyes with tissue damage.

2. Long-term Exposure: Prolonged or repeated contact with o-dichlorobenzene may cause skin irritation. Prolonged or repeated inhalation of high concentrations of vapor might cause liver or kidney injury.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to o-dichlorobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to o-dichlorobenzene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from o-dichlorobenzene exposure.

—Liver disease: o-Dichlorobenzene is known as a liver toxin in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: o-Dichlorobenzene is known as a kidney toxin in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: o-Dichlorobenzene may cause sensitization dermatitis and blistering of the skin . Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

o-Dichlorobenzene vapor at high concentrations is toxic to the liver and kidneys in animals. Rats died from exposure to 977 ppm for 7 hours, but survived when exposed for only 2 hours; animals survived exposure to 539 ppm for 3 hours and at necropsy showed marked centrolobular necrosis of the liver, as well as cloudy swelling of the tubular epithelium of the kidneys. Several species of animals exposed repeatedly to 93 ppm for 7 hours daily showed no adverse effects. The liquid instilled in the rabbit eye produced apparent distress and slight conjunctival irritation. Eye irritation is not

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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usually evident below 20 ppm but becomes noticeable at 25 to 30 ppm and painful to some at 60 to 100 ppm if exposures are for more than a few minutes duration. Some acclimatization may occur, but its extent is not great. Workers exposed daily to an average of 15 ppm showed no indication of injury. The liquid left on the skin may produce blistering. Sensitization dermatitis has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 147
  2. Boiling point (760 mm Hg): 180 C (356 F)
  3. Specific gravity (water = 1): 1.3
  4. Vapor density (air = 1 at boiling point of o-dichlorobenzene): 5.1
  5. Melting point: −17.6 C (0.5 F)
  6. Vapor pressure at 20 C (68 F): 1.2 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
  8. Evaporation rate (butyl acetate = 1): Less than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat.
  2. Incompatibilities: Contact with strong oxidizers or with hot aluminum or aluminum alloys may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, and carbon monoxide) may be released in a fire involving o-dichlorobenzene.
  4. Special precautions: Liquid o-dichlorobenzene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 66 C (151 F) (closed cup)
  2. Autoignition temperature: 648 C (1198 F)
  3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 9.2
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: 2 to 4 ppm, according to the AIHA *Hygienic Guide*; 50 ppm, according to May and Patty.
  2. Eye Irritation Level: 20 to 30 ppm according to the AIHA *Hygienic Guide*.
  3. Evaluation of Warning Properties: Since the odor threshold of o-dichlorobenzene and the concentration causing eye irritation are at or below the permissible exposure, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of o-dichlorobenzene. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure o-dichlorobenzene may be used. An analytical method for o-dichlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6). ical Methods for Set J" (order number PB 263 959).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid o-dichlorobenzene.
- Clothing wet with liquid o-dichlorobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of o-dichlorobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the o-dichlorobenzene, the person performing the operation should be informed of o-dichlorobenzene's hazardous properties.

• Non-impervious clothing which becomes contaminated with liquid o-dichlorobenzene should be removed promptly and not reworn until the o-dichlorobenzene is removed from the clothing.
• Employees should be provided with and required to use splash-proof safety goggles where liquid o-dichlorobenzene may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid o-dichlorobenzene should be promptly washed or showered with soap or mild detergent and water to remove any o-dichlorobenzene.
• Employees who handle liquid o-dichlorobenzene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to o-dichlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in cleaning and degreasing of metal, leather, wool, paper, dry cleaning, brick, and upholstery	General dilution ventilation; personal protective equipment
Use as fumigant for poultry houses and stockyards for termites, moths, and beetles	Personal protective equipment
Use in application or removal of surface coatings	General dilution ventilation; personal protective equipment
Use in maintenance of equipment containing heat-transfer agents	Personal protective equipment
Use in organic synthesis in pesticides, herbicides, dyestuffs, and pharmaceuticals; chemical intermediate in manufacture of toluene-diisocyanate and extractive distillation of ethyl benzene from xylene; use as a deodorizing agent	General dilution ventilation
Use in textile dyeing operations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.
• **Eye Exposure**
If liquid o-dichlorobenzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention. Contact lenses should not be worn when working with this chemical.
• **Skin Exposure**
If liquid o-dichlorobenzene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid o-dichlorobenzene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.
• **Breathing**
If a person breathes in large amounts of o-dichlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
• **Swallowing**
When o-dichlorobenzene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.
• **Rescue**
Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
• If o-dichlorobenzene is spilled or leaked, the following steps should be taken:
1. Remove all ignition sources.

2. Ventilate area of spill or leak.

3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

o-Dichlorobenzene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

2. By atomizing in a suitable combustion chamber equipped with an effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR o-DICHLOROBENZENE

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
1700 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1700 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for p-Dichlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: 1,4-$C_6H_4Cl_2$
- Synonyms: 1,4-Dichlorobenzene; dichlorocide; PDCB
- Appearance and odor: Colorless solid with a mothball-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-dichlorobenzene is 75 parts of p-dichlorobenzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 450 milligrams of p-dichlorobenzene per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Dichlorobenzene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to p-dichlorobenzene may cause irritation of the eyes, nose, and throat. It may also cause headache, swelling around the eyes, and runny nose. In addition, it may cause loss of appetite, nausea, vomiting, weight loss, and liver damage with yellow jaundice and death. Particles of solid p-dichlorobenzene in contact with the eyes may cause pain. The solid material also produces a burning sensation when held in contact with the skin with slight irritation. Warm fumes or strong solutions of p-dichlorobenzene may irritate the skin slightly on prolonged or repeated contact. Red blotching of the skin due to allergy to p-dichlorobenzene may occur.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to p-dichlorobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-dichlorobenzene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver, respiratory tract, eyes, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Since liver damage has been observed in humans exposed to p-dichlorobenzene, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Measurement of 2,5-dichlorophenol may serve as an index of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

p-Dichlorobenzene vapor irritates the eyes and upper respiratory tract and is toxic to the liver. A group of animals repeatedly exposed to 798 ppm developed eye irritation, marked tremors, weakness, and loss of weight; some died. Reversible, nonspecific changes in the eye grounds were noted in rabbits, but there were no lens changes; other effects were centrolobular necrosis of the liver and mild damage to the lungs and kidneys. In five cases of intoxication from exposure to p-dichlorobenzene used as a mothproofing agent, one person with only moderate exposure complained of severe headache, periorbital swelling, and profuse rhinitis, which subsided 24 hours after cessation of exposure.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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The other four persons who had more prolonged exposure developed anorexia, nausea, vomiting, weight loss, and hepatic necrosis with jaundice; two died, and another developed cirrhosis. In 58 workers exposed for an average of 4.8 years (range, 8 months to 25 years) to p-dichlorobenzene at levels of 10 to 725 ppm, there was no evidence of hematologic effects; painful irritation of the eyes and nose was recorded at levels between 50 and 80 ppm, and it was severe at 160 ppm. Solid particles of p-dichlorobenzene in the human eye cause pain. The solid material produces a burning sensation when held in contact with the skin, but the resulting irritation is slight; warm fumes or strong solutions may irritate the intact skin slightly on prolonged or repeated contact. A case of allergic purpura induced by p-dichlorobenzene has been reported. In a study of workers engaged in synthesizing or otherwise handling p-dichlorobenzene, it was concluded that urinary excretion of 2,5-dichlorophenol (a metabolite of paradichlorobenzene) can serve as an index of exposure. Published studies of tests for carcinogenicity are considered to have been too short in duration and involved too few animals to have any significance.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 147
  2. Boiling point (760 mm Hg): 174 C (345 F)
  3. Specific gravity (water = 1): 1.46
  4. Vapor density (air = 1 at boiling point of p-dichlorobenzene): 5.1
  5. Melting point: 53 C (127 F)
  6. Vapor pressure at 20 C (68 F): 0.4 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.008
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving p-dichlorobenzene.
  4. Special precautions: Liquid p-dichlorobenzene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 65.6 C (150 F) (closed cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: 2.5 (calculated at flash point)
  4. Extinguishant: Foam, carbon dioxide, dry chemical
- **Warning properties**
  1. Odor Threshold: Patty states that "p-dichlorobenzene has a very distinctive aromatic odor. The threshold of detection will vary from 15 to 30 ppm in air. The odor becomes very strong at concentrations between 30 and 60 ppm .... It should be recognized, however, that a person may become sufficiently accustomed to the odor to tolerate high concentrations."
  2. Irritation Levels: Patty states that p-dichlorobenzene "is painful to the eyes and nose at concentrations of 80 to 160 ppm. Above 160 ppm, it is intolerable to any person who has not worked in it long enough to have had some adaptation."
  3. Evaluation of Warning Properties: Through its odor and irritant effects, p-dichlorobenzene can be detected within three times the permissible exposure limit. For the purposes of this guideline, therefore, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure p-dichlorobenzene may be used. An analytical method for p-dichlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid particles or vapors from the surface of hot p-dichlorobenzene.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where p-dichlorobenzene or liquids containing p-dichlorobenzene may contact the eyes.

SANITATION

• Workers subject to skin contact with p-dichlorobenzene should wash any areas of the body which may have contacted p-dichlorobenzene at the end of each work day.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to p-dichlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Formulation for use in moth control; as a deordorant for garbage and rest rooms; as an insecticide for control of fruit borers and ants; use in organic synthesis for preparation of dye intermediates	General dilution ventilation; local exhaust ventilation; personal protective equipment
Manufacture of p-dichlorobenzene	General dilution ventilation; local exhaust ventilation; personal protective equipment
Application as an insecticide, air deordorant, moth and mildew preventive, and household fumigant	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If p-dichlorobenzene or liquids containing p-dichlorobenzene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If p-dichlorobenzene or liquids containing p-dichlorobenzene get on the skin, wash the contaminated skin using soap or mild detergent and water. If p-dichlorobenzene or liquids containing p-dichlorobenzene penetrate through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of p-dichlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When p-dichlorobenzene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If p-dichlorobenzene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dispose in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device as in below or deposit in a secured sanitary landfill.

• Waste disposal methods:

p-Dichlorobenzene may be disposed of:

1. By making packages of p-dichlorobenzene in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving p-dichlorobenzene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

3. By disposal in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR p-DICHLOROBENZENE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
1,000 ppm or less	A chemical cartridge respirator with a full facepiece, an organic vapor cartridge(s), and dust filter. A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.