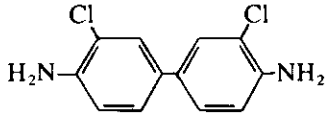
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 3,3′-DICHLOROBENZIDINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 3,3′-dichlorobenzidine 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 Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.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:** $C_{12}H_{10}Cl_2N_2$
- **Structure:**



- **Synonyms:** DCB; 4,4′-diamino-3,3′-dichlorobiphenyl; dichlorobenzidine; o,o′-dichlorobenzidine; 3,3′-dichlorobiphenyl-4,4′diamine
- **Identifiers:** CAS 91-94-1; RTECS DDO525000; DOT not assigned.
- **Appearance:** Gray to purple crystalline solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 253.43
2. Melting point: 133°C (271.4°F)
3. Slightly soluble in water

- **Flammability**

Extinguishant: Dry chemical, alcohol foam, or 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 3,3′-dichlorobenzidine; however, the OSHA standard requires implementation of stringent controls wherever 3,3′-dichlorobenzidine or solid or liquid mixtures containing at least 0.1% by weight or volume of 3,3′-dichlorobenzidine 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 1910.1007, 3,3′-Dichlorobenzidine (and its salts). The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated 3,3′-dichlorobenzidine as an A2 substance (suspected human carcinogen) without having sufficient evidence to assign a threshold limit value (TLV®) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route, including the mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

3,3′-Dichlorobenzidine may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of 3,3′-dichlorobenzidine by rats caused irritation and moderate pulmonary congestion. Chronic oral administration of 3,3′-dichlorobenzidine to rats produced gastrointestinal congestion and hemorrhage, leukemia, and cancers of the intestines and mammary and sebaceous glands. Chronic oral administration of 3,3′-dichlorobenzidine produced bladder cancer in hamsters, liver cancer in mice, and liver and bladder cancers in dogs. 3,3′-Dichlorobenzidine exposure to pregnant mice caused an increased incidence of tumors in their offspring.
2. *Effects on humans:* No reports have been identified that associate 3,3′-dichlorobenzidine with the occurrence of cancer in man; however, because 3,3′-dichlorobenzidine and benzidine (a human bladder carcinogen) are usually prepared and handled in the same workplace, 3,3′-dichlorobenzidine may contribute to the incidence of bladder cancer in exposed workers.

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• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 3,3'-dichlorobenzidine can cause allergic skin reaction, dermatitis, headache, and dizziness. It can also cause severe eye irritation and is caustic to the skin.

2. *Long-term (chronic):* Exposure to 3,3'-dichlorobenzidine can cause blood in the urine and painful, difficult, or frequent 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 3,3'-dichlorobenzidine, 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 hematopoietic (blood-cell-forming) 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 3,3'-dichlorobenzidine 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 liver or urinary tract.

• **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 3,3'-dichlorobenzidine. 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, urinary tract, and hematopoietic and respiratory systems 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. 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 3,3'-dichlorobenzidine 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

• **Method**

Sampling and analysis may be performed by collecting 3,3'-dichlorobenzidine dust with glass-fiber filters and silica gel tubes followed by desorption with triethylamine in methanol and analysis by high-pressure liquid chromatography and ultraviolet detection. Direct-reading devices calibrated to measure 3,3'-dichlorobenzidine may also be used if available. A detailed sampling and analytical method for 3,3'-dichlorobenzidine may be found in the *NIOSH Manual of Analytical Methods* (method number 5509).

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 3,3'-dichlorobenzidine 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 3,3'-dichlorobenzidine 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 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 3,3'-dichlorobenzidine 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 3,3'-dichlorobenzidine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 3,3'-dichlorobenzidine'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 3,3'-dichlorobenzidine 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 1910.1007:

Areas where 3,3'-dichlorobenzidine 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 are 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 3,3'-dichlorobenzidine, 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 3,3'-dichlorobenzidine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 3,3'-dichlorobenzidine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 3,3'-dichlorobenzidine 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 3,3'-dichlorobenzidine 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 man-

ner that does not cause contamination of nonregulated areas or the external environment.

Decontamination procedures shall be established and implemented to remove 3,3'-dichlorobenzidine from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 3,3'-dichlorobenzidine 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 3-3'-dichlorobenzidine

Operations	Controls
During use as an intermediate in the manufacture of dyes, pigments, and isocyanate-containing polymers	Process enclosure, restricted access, local exhaust ventilation where appropriate, 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 had contact with 3,3'-dichlorobenzidine, 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 3,3'-dichlorobenzidine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 3,3'-dichlorobenzidine 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 3,3'-dichlorobenzidine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 3,3'-dichlorobenzidine gets on the skin, wash it immediately with soap and water. If 3,3'-dichlorobenzidine 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 3,3'-dichlorobenzidine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, 3,3'-dichlorobenzidine may be collected and placed in an appropriate container.
3. 3,3'-Dichlorobenzidine solid or liquid 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 3,3'-dichlorobenzidine are prohibited by OSHA.
4. For small quantities of liquids containing 3,3'-dichlorobenzidine, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing 3,3'-dichlorobenzidine 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 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 respira-

tor, 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 3-3′-dichlorobenzidine

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 Dichlorodifluoromethane

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: CCl_2F_2
- Synonyms: Refrigerant 12; Freon 12; propellant 12; Halon 122
- Appearance and odor: Colorless gas with a characteristic ether-like odor that is detectable only in concentrations well above the permissible exposure (above 20% by volume).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dichlorodifluoromethane is 1000 parts of dichlorodifluoromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 4950 milligrams of dichlorodifluoromethane per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dichlorodifluoromethane 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: Exposure to dichlorodifluoromethane may cause dizziness, involuntary trembling, unconsciousness, and death. It may also cause irregular heartbeat. If the liquid gets on the skin or in the eyes, it may cause frostbite.

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 dichlorodifluoromethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dichlorodifluoromethane 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 dichlorodifluoromethane exposure.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of dichlorodifluoromethane might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Dichlorodifluoromethane vapor is a narcotic and can cause asphyxia at very high concentrations. At 800,000 ppm rats were deeply anesthetized, but 4 to 6 hours' exposure produced no permanent effects. At 200,000 ppm dogs and monkeys showed only tremors, salivation, and lacrimation. Inhalation by man at 150,000 ppm produces unconsciousness, while dizziness occurs at 50,000 ppm. Sniffing aerosols of fluorochlorinated hydrocarbons has caused sudden death by cardiac arrest, probably due to sensitization of the myocardium. In liquid form this substance may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 120.9
2. Boiling point (760 mm Hg): −29.8 C (−21.6 F)
3. Specific gravity (water = 1): 1.49 (at boiling

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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point)

4. Vapor density (air = 1 at boiling point of dichlorodifluoromethane): 4.2

5. Melting point: −157.7 C (−252 F)

6. Vapor pressure at 20 C (68 F): 5.7 atm.

7. Solubility in water, g/100 g water at 20 C (68 F): 0.008

8. Evaporation rate (butyl acetate = 1): 380

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Dichlorodifluoromethane reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and hydrogen fluoride) may be released when dichlorodifluoromethane decomposes.

4. Special precautions: Liquid dichlorodifluoromethane will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Since dichlorodifluoromethane is practically odorless and is not an irritant, it is treated as a material with poor warning properties.

Grant states that "in ordinary occupational or domestic exposure to the gas, there is neither ocular nor respiratory irritation. Dogs, monkeys, and guinea pigs exposed to 20% of the gas in air for several hours a day for several days showed temporary intoxication with tremors, ataxia, and associated tendency to stare, salivate, and lacrimate, but no cumulative toxic effect and no specific ocular disturbance. The speed of reflex closure of the eyes is such that it seems extremely unlikely that any seriuos injury would result from an accidental spray of this substance in the eyes of human beings."

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 dichlorodifluoromethane 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).

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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 wet with liquid dichlorodifluoromethane or from becoming frozen from contact with vessels containing dichlorodifluoromethane.

• Any clothing which becomes wet with liquid dichlorodifluoromethane should be removed immediately and not reworn until the dichlorodifluoromethane has evaporated from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid dichlorodifluoromethane may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dichlorodifluoromethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of aerosols for cosmetics,	General dilution ventilation; personal

pharmaceuticals, insecticides, paints, adhesives, and cleaners; use in manufacture and extensive use as a refrigerant in home and commercial applications	protective equipment
Use as a blowing agent for cellular polymers; use as a solvent or diluent in fumigants for food sterilization; in paints and varnish removers, and in polymerization processes	General dilution ventilation; personal protective equipment
Use as a foaming agent in fire extinguishing, aerosols, for surfactants; use in Immersion Quick Freezing of food products	General dilution ventilation; personal protective equipment
Use in water purification; copper and aluminum purification, petroleum recovery, and in manufacture of glass bottles	General dilution ventilation; personal protective equipment
Use in regulating devices for leak detection; in thermal expansion valves; use in manufacture of materials for electrical applications as insulators and generator windings	General dilution ventilation; personal protective equipment
Use in organic synthesis of Freons, and a polymerization catalysts; use as a working fluid for heat pumps and in hydraulic fluids	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 dichlorodifluoromethane 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 liquid dichlorodifluoromethane gets on the skin, immediately flush the skin with water if the dichlorodifluoromethane has not already evaporated. If liquid dichlorodifluoromethane soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for flushing. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of dichlorodifluoromethane, 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 LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If dichlorodifluoromethane is leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. Stop flow of gas.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Dichlorodifluoromethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Material Safety Data Sheet – Dichlorodifluoromethane*, New York, 1972.

RESPIRATORY PROTECTION FOR DICHLORODIFLUOROMETHANE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Gas Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50,000 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 with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
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 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 1,3-Dichloro-5,5-Dimethylhydantoin

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: $C_5H_6Cl_2N_2O_2$
- Synonyms: Halane; dactin
- Appearance and odor: White solid with a chlorine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,3-dichloro-5,5-dimethylhydantoin is 0.2 milligram of 1,3-dichloro-5,5-dimethylhydantoin per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,3-Dichloro-5,5-dimethylhydantoin 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: This chemical is a chlorine bleach which is activated by moisture and may irritate the eyes, nose, throat, lungs, and skin.

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 1,3-dichloro-5,5-dimethylhydantoin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,3-dichloro-5,5-dimethylhydantoin 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 1,3-dichloro-5,5-dimethylhydantoin exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,3-dichloro-5,5-dimethylhydantoin 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**

1,3-Dichloro-5,5-dimethylhydantoin powder in contact with water yields hypochlorous acid, which is an eye and mucous membrane irritant. The LD50 for rats, when administered orally as a 10% aqueous suspension, was 542 mg/kg; at necropsy, gastrointestinal hemorrhages were found. There is a single report of workmen exposed to an average concentration of 1.97 mg/m^3 experiencing marked respiratory irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 197
2. Boiling point (760 mm Hg): Not available
3. Specific gravity (water = 1): 1.5
4. Vapor density (air = 1 at boiling point of 1,3-dichloro-5,5-dimethylhydantoin): 6.8
5. Melting point: 130 C (266 F)
6. Vapor pressure at 20 C (68 F): Not available
7. Solubility in water, g/100 g water at 20 C (68 F): 0.20
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Dry 1,3-

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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dichloro-5,5-dimethylhydantoin decomposes with formation of toxic gases at 202– 210 C (395– 410 F). If material is wet, it will decompose at lower temperatures.

2. Incompatibilities: Contact with water, strong acids, and easily oxidized materials such as ammonium salts, sulfides, etc., may cause fires and explosions and formation of toxic fumes of chlorine and nitrogen trichloride.

3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine, hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,3-dichloro-5,5-dimethylhydantoin.

4. Special precautions: 1,3-Dichloro-5,5-dimethylhydantoin will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 174 C (346 F)
2. Autoignition temperature: Not available
3. Flammable limits in air, % by volume: Not available
4. Extinguishant: Carbon dioxide, dry chemical

• **Warning properties**

1,3-Dichloro-5,5-dimethylhydantoin is a powder, but in the presence of moisture chlorine gas is released. May states that the odor threshold of chlorine is .01 ppm, which is well below the permissible exposure of 1 ppm. Chlorine has adequate warning properties.

Stecher reports that the chlorine liberated upon the decomposition of 1,3-dichloro-5,5-dimethylhydantoin may produce irritation of the eyes and mucous membranes. Patty reports that men can work without interruption in an environment containing 3 to 6 mg/m^3 of chlorine, but exposures to concentrations of 10 to 20 mg/m^3 causes "a stinging or burning sensation in the eyes . . . ." Eye protection is recommended for any possibility of contact in the personal protection section.

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 1,3-dichloro-5,5-dimethylhydantoin 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 repeated or prolonged skin contact with solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin.

• If employees' clothing may have become contaminated with solid 1,3-dichloro-5,5-dimethylhydantoin, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,3-dichloro-5,5-dimethylhydantoin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,3-dichloro-5,5-dimethylhydantoin, the person performing the operation should be informed of 1,3-dichloro-5,5-dimethylhydantoin's hazardous properties.

• Non-impervious clothing which becomes contaminated with solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin should be removed promptly and not reworn until the 1,3-dichloro-5,5-dimethylhydantoin 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 solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin should be promptly washed or showered with soap or mild detergent and water to remove any 1,3-dichloro-5,5-dimethylhydantoin.

• Employees who handle solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin 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 1,3-dichloro-5,5-dimethylhydantoin may occur and control methods which may be effective in each case:

Operation	Controls
Use as a bactericide, sporicide, or sanitizer in swimming pools, dairies, laundries, restaurants, cutting oils, and pharmaceutical industry; as a general cleaner	General dilution ventilation; personal protective equipment
Use as a mild chlorinating agent in organic synthesis	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during use as a rubber retarder	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a bleaching agent in commercial laundries	General dilution ventilation; personal protective equipment
Use as stabilizer, discoloration preventer, and catalyst in polymer industry; use to emboss or texturize resinous sheet preparations	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 1,3-dichloro-5,5-dimethylhydantoin 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 solid or liquids containing 1,3-dichloro-5,5-dimethylhydantoin get on the skin, promptly flush the contaminated skin using soap or mild detergent and water. If liquids containing 1,3-dichloro-5,5-dimethylhydantoin soak through the clothing, remove the clothing promptly and flush 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 1,3-dichloro-5,5-dimethylhydantoin, 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 1,3-dichloro-5,5-dimethylhydantoin 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 1,3-dichloro-5,5-dimethylhydantoin is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. 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.) Small quantities may also be slowly added to large amounts of water and flushed into a sewer. 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:

1,3-Dichloro-5,5-dimethylhydantoin may be disposed of:

1. By making packages of 1,3-dichloro-5,5-dimethylhydantoin in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. By dissolving 1,3-dichloro-5,5-dimethylhydantoin in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. Small quantities may be slowly added to large amounts of water and flushed into a sewer.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "1,3-Dichloro-5,5-Dimethylhydantoin," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR 1,3-DICHLORO-5,5-DIMETHYLHYDANTOIN

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any chemical cartridge respirator with a full facepiece, chlorine cartridge(s), and dust filter(s).
	A gas mask with a chin-style or a front- or back-mounted chlorine 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 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 chlorine and particulates.
	Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for 1,1-Dichloroethane

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_3CHCl_2
- Synonyms: Asymmetrical dichloroethane; ethylidene chloride; 1,1-ethylidene dichloride
- Appearance and odor: Colorless liquid with a chloroform-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1-dichloroethane is 100 parts of 1,1-dichloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 400 milligrams of 1,1-dichloroethane per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for 1,1-dichloroethane a Threshold Limit Value of 200 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1-Dichloroethane 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: Breathing 1,1-dichloroethane vapor may cause drowsiness and unconsciousness. It might also cause damage to the liver, kidneys, and lungs. Splashing the liquid in the eyes may cause irritation.

2. Long-term Exposure: Prolonged, confined, or repeated skin contact with 1,1-dichloroethane can produce a slight burn.

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 1,1-dichloroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1-dichloroethane 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 1,1-dichloroethane exposure.

—Skin disease: 1,1-Dichloroethane 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 1,1-dichloroethane 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 1,1-dichloroethane 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 1,1-dichloroethane 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**

1,1-Dichloroethane vapor is a narcotic. Rats exposed to 32,000 ppm for 30 minutes did not survive. The most consistent findings in animals exposed to concentrations

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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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of above 8,000 ppm for up to 7 hours were pathologic changes in the kidney and liver, and at much higher concentrations, near 64,000 ppm, damage to the lungs as well. Repeated daily exposure of several species of animals to 1,000 ppm resulted in no pathologic or hematologic changes. The liquid applied to the intact or abraded skin of rabbits produced slight edema and very slight necrosis after six daily applications. Instilled in the eyes of rabbits there was immediate, moderate conjunctival irritation and swelling which subsided within a week. There have been no reported cases of human overexposure by inhalation; prolonged, confined, or repeated skin contact can produce a slight burn.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 99
2. Boiling point (760 mm Hg): 57.3 C (135 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of 1,1-dichloroethane): 3.4
5. Melting point: −96.7 C (−142 F)
6. Vapor pressure at 20 C (68 F): 182 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.1
8. Evaporation rate (butyl acetate = 1): 11.6

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong caustics will cause formation of flammable and toxic acetaldehyde gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as vinyl chloride, hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,1-dichloroethane.
4. Special precautions: 1,1-Dichloroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −8.5 C (17 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 5.9; Upper: 15.9
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

The AIHA *Hygienic Guide* reports that 1,1-dichloroethane has a distinctive, easily recognizable odor at the TLV.

1,1-Dichloroethane 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 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 1,1-dichloroethane may be used. An analytical method for 1,1-dichloroethane 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 1,1-dichloroethane.
- Clothing wet with liquid 1,1-dichloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1-dichloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1-dichloroethane, the person performing the operation should be informed of 1,1-dichloroethane's hazardous properties.
- Any clothing which becomes wet with liquid 1,1-dichloroethane should be removed immediately and not

reworn until the 1,1-dichloroethane is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid 1,1-dichloroethane may contact the eyes.

SANITATION

• Skin that becomes wet with liquid 1,1-dichloroethane should be immediately washed or showered with soap or mild detergent and water to remove any 1,1-dichloroethane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1-dichloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as dewaxer of mineral oils; extractant for heat-sensitive substances	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a fumigant	General dilution ventilation of work area; personal protective equipment
Use in manufacture of vinyl chloride by vapor phase cracking; use in manufacture of high vacuum rubber and silicon grease; use as a chemical intermediate	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 1,1-dichloroethane 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 1,1-dichloroethane gets on the skin, promptly flush the contaminated skin using soap or mild detergent and water. If 1,1-dichloroethane soaks through the clothing, remove the clothing immediately and flush 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 1,1-dichloroethane, 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 1,1-dichloroethane 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 1,1-dichloroethane 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. 1,1-Dichloroethane 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 1,1-dichloroethane vapors are permitted.

• Waste disposal method:

1,1-Dichloroethane may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR 1,1-DICHLOROETHANE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
4000 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. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 4000 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 1,2-Dichloroethylene

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=CHCl
- Synonyms: Acetylene dichloride; dioform; trans-acetylene dichloride; sym-dichloroethylene
- Appearance and odor: Colorless liquid with an ether-like, slightly acrid odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,2-dichloroethylene is 200 parts of 1,2-dichloroethylene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 790 milligrams of 1,2-dichloroethylene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,2-Dichloroethylene 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 1,2-dichloroethylene may cause dizziness, drowsiness, and unconsciousness.

- **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 1,2-dichloroethylene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,2-dichloroethylene 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 1,2-dichloroethylene exposure.

—Liver disease: Although 1,2-dichloroethylene 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.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,2-dichloroethylene 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**

1,2-Dichloroethylene vapor is a narcotic and a mucous-membrane irritant. Variations in toxicity of the cis- as compared with the trans-form have been reported. A concentration of 39,000 ppm was lethal to guinea pigs, and narcosis was produced at 18,000 ppm. Dogs exposed to high concentrations of vapor developed superficial corneal turbidity which was reversible. No effects were observed in several species with repeated exposure for up to 6 months at 1000 ppm. It has been used as a general anesthetic in man; one industrial fatality was due to very high vapor inhalation in a small enclosure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 96.9
2. Boiling point (760 mm Hg): 45 to 60 C (113 to 140 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of 1,2-dichloroethylene): 3.34
5. Melting point: −49 to −81.5 C (−56 to −115 F)
6. Vapor pressure at 20 C (68 F): 180 to 265 mm Hg

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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7. Solubility in water, g/100 g water at 20 C (68 F): 0.35 to 0.63

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 hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,2-dichloroethylene.

4. Special precautions: 1,2-Dichloroethylene will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 2.2 to 3.9 C (36 to 39 F) (closed cup)

2. Autoignition temperature: 460 C (860 F) for trans-1,2-dichloroethylene

3. Flammable limits in air, % by volume: Lower: 9.7; Upper: 12.8

4. Extinguishant: Dry chemical, foam, carbon dioxide

• **Warning properties**

May reports an odor threshold of 0.085 ppm for dichloroethylene. For the purposes of this guideline, 1,2-dichloroethylene is treated as a material with adequate warning properties.

1,2-Dichloroethylene is an eye irritant, according to Grant, but the concentrations at which irritation occurs 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 1,2-dichloroethylene 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 1,2-dichloroethylene may be used. An analytical method for 1,2-dichloroethylene 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 1,2-dichloroethylene.

• Clothing wet with liquid 1,2-dichloroethylene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,2-dichloroethylene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,2-dichloroethylene, the person performing the operation should be informed of 1,2-dichloroethylene's hazardous properties.

• Any clothing which becomes wet with liquid 1,2-dichloroethylene should be removed immediately and not reworn until the 1,2-dichloroethylene is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid 1,2-dichloroethylene may contact the eyes.

SANITATION

• Skin that becomes wet with liquid 1,2-dichloroethylene should be promptly washed or showered with soap or mild detergent and water to remove any 1,2-dichloroethylene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,2-dichloroethylene may occur and control methods which may be effective in each case:

Operation	Controls
Use as a low-temperature solvent for heat-sensitive substances in extraction of caffeine, perfume oils, and fats from flesh of animals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber and dye industries in extraction and application	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a direct solvent in gums, waxes, oils, camphor, and phenol; use in solvent mixtures for esters and ether derivatives, lacquers, resins, thermoplastics, and artificial fibers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for polymers and telomers	Process enclosure; local exhaust ventilation; personal protective equipment
Use in miscellaneous applications as liquid dry cleaning agent, cleaning solution for printed circuit boards, food packaging adhesives, and germicidal fumigants	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 1,2-dichloroethylene 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 1,2-dichloroethylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,2-dichloroethylene 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 1,2-dichloroethylene, 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 1,2-dichloroethylene 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 1,2-dichloroethylene 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. 1,2-Dichloroethylene 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 1,2-dichloroethylene vapors are permitted.

- Waste disposal method:

1,2-Dichloroethylene may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "1.2-Dichloroethylene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR 1,2-DICHLOROETHYLENE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
4000 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 4000 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 Dichloroethyl Ether

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: $(ClCH_2CH_2)_2O$
- Synonyms: Bis(2-chloroethyl)ether;2,2'-dichlorodiethyl ether
- Appearance and odor: Colorless liquid with a chlorinated solvent-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dichloroethyl ether is a ceiling level of 15 parts of dichloroethyl ether per million parts of air (ppm). This may also be expressed as 90 milligrams of dichloroethyl ether per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for dichloroethyl ether a Threshold Limit Value of 5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dichloroethyl ether 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: Exposure to dichloroethyl ether vapor may cause severe irritation of the eyes and nose with coughing, retching, and nausea. In animal experiments, dichloroethyl ether has caused severe irritation of the respiratory tract with severe breathing difficulties which can be delayed in onset. Animal experiments have also shown dichloroethyl ether vapor to be capable of causing drowsiness, dizziness, and unconsciousness at high concentrations. Liquid dichloroethyl ether placed in animal eyes has produced damage. Feeding this chemical to mice has been associated with an increased amount of liver tumors.

2. Long-term Exposure: Repeated exposure to dichloroethyl ether may cause 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 dichloroethyl ether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dichloroethyl ether 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 tract, liver, and the central nervous system should be stressed.

—14" x 17" chest roentgenogram: Dichloroethyl ether causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Dichloroethyl ether is a severe pulmonary irritant in animals. 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 signs and symptoms of respiratory disease.

- **Summary of toxicology**

Dichloroethyl ether vapor is a severe respiratory irritant; high levels cause narcosis in animals. It is tumorigenic in animals. Repeated oral administration of 100 mg/kg daily to both sexes of two strains of mice for 80 weeks induced a significantly elevated incidence of tumors, mostly hepatomas. In guinea pigs, concentrations of 500 to 1000 ppm were fatal after 5 to 8 hours of

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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exposure; there were immediate lacrimation and nasal irritation, followed by unsteadiness and coma; autopsy findings were pulmonary edema, hemorrhage and occasional complete consolidation. In experimental human exposure, 500 ppm caused intolerable irritation to the eyes and nose with cough, nausea and vomiting; at 100 ppm there was some irritation, while at 35 ppm there were no effects. Except for accidental inhalation of high concentrations, the chief hazard in industrial practice is mild bronchitis, which may be caused by repeated exposures to low concentrations. Both the liquid and a 10% solution dropped in the eye of a rabbit caused moderate discomfort, conjunctival irritation, and corneal injury which generally healed within 24 hours. On the skin of rabbits, the pure liquid had no local effect, but a sufficient amount penetrated the skin to cause death within a day.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 143
2. Boiling point (760 mm Hg): 178.2 C (353 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of dichloroethyl ether): 4.9
5. Melting point: −52 C (−62 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): 1.1
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: At elevated temperatures containers may burst.
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 dichloroethyl ether.
4. Special precautions: Dichloroethyl ether will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 55 C (131 F) (closed cup)
2. Autoignition temperature: 369 C (696 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: According to Patty, "most people can detect the chemical at its threshold limit (15 ppm) by its odor."
2. Irritation Levels: Patty states that "Schrenk, Patty, and Yant exposed human volunteers to dichloroethyl ether. Brief exposure to concentrations above 550 ppm were very irritating to the eyes and nasal passages and were considered intolerable. They also caused coughing, retching, and nausea. At 260 and 100 ppm the irritating effects were still present to some extent but were not considered intolerable."
3. Evaluation of Warning Properties: Through its odor dichloroethyl ether can be detected at the permissible exposure limit. For the purposes of this guideline, therefore, dichloroethyl ether is treated as a substance 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 dichloroethyl ether. 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 dichloroethyl ether may be used. An analytical method for dichloroethyl ether 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 dichloroethyl ether, where skin contact may occur.
• Clothing contaminated with dichloroethyl ether should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dichloroethyl ether from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dichloroethyl ether, the person performing the operation should be informed of dichloroethyl ether's hazardous properties.
• Where exposure of an employee's body to liquid dichloroethyl ether 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 dichloroethyl ether should be removed immediately and not reworn until the dichloroethyl ether is removed from the clothing.
• Employees should be provided with and required to use splash-proof safety goggles where liquid dichloroethyl ether may contact the eyes.

SANITATION

• Skin that becomes contaminated with dichloroethyl ether should be immediately washed or showered with soap or mild detergent and water to remove any dichloroethyl ether.
• Employees who handle dichloroethyl ether 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 dichloroethyl ether may occur and control methods which may be effective in each case:

Operation	Controls
Use as solvent, dewaxing agent in petroleum industry and manufacture of oils, fats, waxes, gums, tars, resins, soaps, ethyl cellulose, paints, varnish, and lacquers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as scouring and penetrating agent in textile industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as fumigant in agricultural insecticide industry	Personal protective equipment
Use as chemical intermediate in synthesis during manufacture of pharmaceuticals, rubber chemicals, resins, plasticizers, and chemicals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as lead scavenger during production of gasoline engine anti-knock compounds	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 dichloroethyl ether 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 liquid dichloroethyl ether gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid dichloroethyl ether 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 dichloroethyl ether, 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 dichloroethyl ether 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 dichloroethyl 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, 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. Dichloroethyl ether should not be allowed to enter a confined space, such as sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of dichloroethyl ether vapors are permitted.
• Waste disposal methods:
Dichloroethyl ether 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.

ADDITIONAL INFORMATION

To find additional information on dichloroethyl ether, look up dichloroethyl ether 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 9, 1975.

RESPIRATORY PROTECTION FOR DICHLOROETHYL ETHER

Condition	Minimum Respiratory Protection* Required Above 15 ppm
Vapor Concentration	
150 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).** Any supplied-air respirator.** Any self-contained breathing apparatus.**
250 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.
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.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of dichloroethyl ether; 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 250 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Dichloromonofluoromethane (Refrigerant 21)

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: $CHCl_2F$
- Synonyms: Refrigerant 21; Freon 21; Halon 112; dichlorofluoromethane
- Appearance and odor: Colorless liquid or gas with a slight ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Refrigerant 21 is 1000 parts of Refrigerant 21 per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 4200 milligrams of Refrigerant 21 per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Refrigerant 21 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 Refrigerant 21 may cause drowsiness, unconsciousness, and death. Exposure to Refrigerant 21 may cause the heart to beat irregularly. If the liquid is spilled on the skin, it may cause frostbite.

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 Refrigerant 21.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Refrigerant 21 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 Refrigerant 21 exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Refrigerant 21 might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of Refrigerant 21 might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Refrigerant 21 vapor is a respiratory irritant and causes asphyxia at extremely high concentrations. Exposure to 400,000 ppm with 18% oxygen was fatal to guinea pigs; death was preceded by dyspnea, tremors, and convulsive movements but not narcosis. Animals died at 102,000 ppm with congested lungs, kidneys, and liver, but survived 52,000 ppm showing tremors, incoordination, and irregular breathing. In liquid form this substance may cause frostbite. Sniffing aerosols of fluorochlorinated hydrocarbons has caused sudden death by cardiac arrest, probably due to sensitization of the myocardium. Acute or chronic effects from human exposure have not been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.9

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): 8.9 C (48.1 F)
3. Specific gravity (water = 1): 1.37
4. Vapor density (air = 1 at boiling point of Refrigerant 21): 3.82
5. Melting point: −135 C (−211 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): 1
8. Evaporation rate (butyl acetate = 1): Much higher than 1

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Refrigerant 21 reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and hydrogen fluoride) may be released when Refrigerant 21 decomposes.
4. Special precautions: Liquid Refrigerant 21 will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Since there is no available quantitative information relating warning properties to air concentrations of Refrigerant 21, this substance is treated as a material with poor warning properties.
Refrigerant 21 is not a known 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 Refrigerant 21 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 the skin from becoming wet with liquid Refrigerant 21.

• Any clothing which becomes wet with liquid Refrigerant 21 should be removed immediately and not reworn until the Refrigerant 21 has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid Refrigerant 21 may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Refrigerant 21 may occur and control methods which may be effective in each case:

Operation	Controls
Manufacture and use as an aerosol propellant in pharmaceuticals; use as a refrigerating agent; use as an industrial solvent in separation of fatty acids, of polymers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a blowing agent for rigid foams and insulating foams	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a working fluid in Rankine cycle turbogenerators; use in water purification; use in organic synthesis in preparation of other Freons	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 Refrigerant 21 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 liquid Refrigerant 21 gets on the skin, immediately flush the contaminated skin with water if the Refrigerant 21 has not already evaporated. If liquid Refrigerant 21 soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of Refrigerant 21, 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 Refrigerant 21 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 until cleanup has been completed.

• If Refrigerant 21 is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If the gas is leaking, stop the flow.
3. If the liquid is spilled or leaked, allow to vaporize.

REFERENCES

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RESPIRATORY PROTECTION FOR REFRIGERANT 21

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Gas Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50,000 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 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 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 1,1-Dichloro-1-Nitroethane

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: $CH_3CCl_2NO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with an unpleasant odor that causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1-dichloro-1-nitroethane is a ceiling of 10 parts of 1,1-dichloro-1-nitroethane per million parts of air (ppm). This may also be expressed as 60 milligrams of 1,1-dichloro-1-nitroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1-Dichloro-1-nitroethane 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 of animals has produced severe irritation of the lungs with severe breathing difficulties. These breathing difficulties may be delayed in onset. Liver, heart, kidney, and blood vessel damage were also reported in animals. In addition, eye and skin irritation have 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 1,1-dichloro-1-nitroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1-dichloro-1-nitroethane 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 1,1-dichloro-1-nitroethane exposure.

—Chronic respiratory disease: 1,1-Dichloro-1-nitroethane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,1-dichloro-1-nitroethane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: 1,1-Dichloro-1-nitroethane 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: 1,1-Dichloro-1-nitroethane 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: 1,1-Dichloro-1-nitroethane causes heart damage in animals. In persons with impaired cardiovascular function, the inhalation of 1,1-dichloro-1-nitroethane might cause exacerbation of preexisting disorders.

—Skin disease: 1,1-Dichloro-1-nitroethane can cause dermatitis on prolonged exposure. Persons with preexisting 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**

1,1-Dichloro-1-nitroethane vapor is a pulmonary, skin, and eye irritant in animals. It also causes liver, kidney, and heart damage in animals. At high concentrations animals showed lacrimation, increased nasal secretion,

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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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sneezing, coughing, pulmonary rales, and weakness. Exposure of rabbits to levels as low as 52 ppm for 18-½ hours was fatal. Autopsies on animals exposed to more than 170 ppm for over 30 minutes revealed pulmonary edema and hemorrhage, with damage to the heart, liver, and kidneys. Application of the liquid to the skin of rabbits caused irritation and edema. No human experience has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 144
2. Boiling point (760 mm Hg): 125 C (257 F)
3. Specific gravity (water = 1): 1.42
4. Vapor density (air = 1 at boiling point of 1,1-dichloro-1-nitroethane): 5.0
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 15 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.25
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 1,1-dichloro-1-nitroethane.
4. Special precautions: Liquid 1,1-dichloro-1-nitroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 58 C (136 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 1,1-dichloro-1-nitroethane.
2. Eye Irritation Level: The *Handbook of Organic Industrial Solvents* states that this substance "may cause irritation of eyes and nose at twice threshold limit and, at higher concentrations, lung injury." Grant points out that it "has an irritant, lacrimogenic effect which gives adequate warning to prevent dangerous exposure."
3. Evaluation of Warning Properties: Although 1,1-dichloro-1-nitroethane produces irritant effects at only twice the permissible exposure limit, it is treated as a substance with poor warning properties, since the permissible exposure limit is a ceiling concentration which was set "to prevent serious injury in man."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of 1,1-dichloro-1-nitroethane. 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 1,1-dichloro-1-nitroethane may be used. An analytical method for 1,1-dichloro-1-nitroethane 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 1,1-dichloro-1-nitroethane.

• Clothing wet with liquid 1,1-dichloro-1-nitroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1-dichloro-1-nitroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1-dichloro-1-nitroethane, the person performing the operation should be informed of 1,1-dichloro-1-nitroethane's hazardous properties.
• Non-impervious clothing which becomes contaminated with 1,1-dichloro-1-nitroethane should be removed promptly and not reworn until the 1,1-dichloro-1-nitroethane is removed from the clothing.
• Employees should be provided with and required to use splash-proof safety goggles where liquid 1,1-dichloro-1-nitroethane may contact the eyes.

SANITATION

• Skin that becomes contaminated with 1,1-dichloro-1-nitroethane should be promptly washed or showered with soap or mild detergent and water to remove any 1,1-dichloro-1-nitroethane.
• Employees who handle liquid 1,1-dichloro-1-nitroethane 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 1,1-dichloro-1-nitroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as an insecticidal fumigant for grain (this product is not in common use at this time)	Material substitution

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 1,1-dichloro-1-nitroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.
• **Skin Exposure**
If liquid 1,1-dichloro-1-nitroethane gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid 1,1-dichloro-1-nitroethane soaks 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 1,1-dichloro-1-nitroethane, 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 1,1-dichloro-1-nitroethane 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 1,1-dichloro-1-nitroethane 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. 1,1-Dichloro-1-nitroethane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
• Waste disposal method:
1,1-Dichloro-1-nitroethane 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 1,1-DICHLORO-1-NITROETHANE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
150 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 150 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 1,3-DICHLOROPROPENE

INTRODUCTION

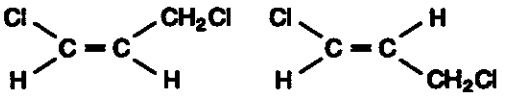
This guideline summarizes pertinent information about 1,3-dichloropropene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations 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**

$C_3H_4Cl_2$

- **Structure**



- **Synonyms**

alpha-Chloroallyl chloride; gamma-chloroallyl chloride; 1,3-dichloropropylene; 1,3-dichloropropene-1; Telone; Telone II; Dorlone; alpha,gamma-dichloropropylene.

- **Identifiers**

1. CAS No.: 542-75-6
2. RTECS No.: UC8310000
3. DOT UN: 2047 29
4. DOT label: Flammable liquid

- **Appearance and odor**

1,3-Dichloropropene is a straw-colored liquid with a chloroform-like odor; the commercial product consists of the cis- and trans-isomers in approximately equal parts.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 110.98
2. Boiling point (760 mm Hg): 103°C (217°F)
3. Specific gravity (water = 1): 1.2 at 20°C (68°F)
4. Vapor density at 37.8°C (100°F): 3.8
5. Freezing point: -84°C (-119.2°F)
6. Vapor pressure at 25°C (77°F): approximately 28 mm Hg

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7. Solubility: Insoluble in water; soluble in acetone, toluene, octane, carbon tetrachloride, n-heptane, methanol, and benzene.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame. The vapors of this substance also form explosive mixtures with air.

2. Incompatibilities: Contact of 1,3-dichloropropene with oxidizers, aluminum or magnesium compounds, or alkaline or corrosive materials causes a violent reaction.

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving 1,3-dichloropropene.

4. Special precautions: This substance can polymerize if not stabilized with epichlorohydrin or another stabilizer.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to 1,3-dichloropropene.

1. Flash point: 35°C (95°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air (% by volume): Lower, 5.3; upper, 14.5

4. Extinguishant: Use water spray, dry chemical, standard foam, or carbon dioxide to fight fires involving 1,3-dichloropropene. 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 1,3-dichloropropene 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 1,3-dichloropropene 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 is 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 half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 1,3-dichloropropene. Structural firefighters' protective clothing may provide limited protection against fires involving 1,3-dichloropropene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 1,3-dichloropropene [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 ppm (5 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, 1,3-dichloropropene 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 1,3-dichloropropene a threshold limit value (TLV) of 1 ppm as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to 1,3-dichloropropene [ACGIH 1991].

- **Rationale for limits**

The NIOSH limit is based on the potential for cancer associated with 1,3-dichloropropene exposure. The ACGIH limit is based on the risk of kidney injury associated with exposure to 1,3-dichloropropene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 1,3-dichloropropene can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to 1,3-dichloropropene irritates the skin, eyes, and mucous membranes and may cause respiratory tract, liver, and kidney damage in experimental animals. 1,3-Dichloropropene is also carcinogenic in rodents. Exposure to 1,3-dichloropropene vapor (concentration and duration not specified) caused moderate to severe conjunctival irritation and slight to moderate reversible corneal injury in rabbits; applied to the skin of animals of the same species, this substance caused swelling and necrosis [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits for the same solution is 504 mg/kg [ACGIH 1991]. The LC_{50} in rats is 500 ppm for an unspecified period of time, while the 2-hr LC_{50} in mice is 1,033 ppm [NIOSH 1993]. The oral LD_{50} for a 10-percent solution of 1,3-dichloropropene (92-percent purity) in corn oil is 713 mg/kg in male rats and 470 mg/kg in female rats [ACGIH 1991]. Acute inhalation exposure (duration not specified) to concentrations above 2,700 ppm irritated the eyes and nose and caused serious injury to the lungs, liver, and kidneys of rats; exposure to a 1,000 ppm concentration for a period described as "brief" caused severe eye irritation and loss of consciousness, while exposure to 1,000 ppm for 2 hours was lethal to all exposed rats [ACGIH 1991]. Exposure to a 3 ppm concentration of 1,3-dichloropropene for 7-hours a day, 5 days a week for 6 months produced reversible swelling of renal tubular epithelium in rats [ACGIH 1991]. Rats and mice exposed to 0, 93, 32, or 12 ppm for 7 hours a day, 5 days a week for 13 weeks experienced growth depression (high dose rats and female mice) and focal changes of the nasal epithelium in high dose rats (both sexes) and female rats exposed to 32 ppm [Clayton and Clayton 1981]. 1,3-Dichloropropene has been tested in oral carcinogenicity bioassays in both mice and rats. In mice, it produced dose-related increases in the incidences of benign and/or malignant tumors of the urinary bladder, lung, and forestomach. In male rats, it caused dose-related increases in the incidences of benign and malignant forestomach tumors and benign liver tumors; in female rats, it produced benign forestomach tumors [IARC 1986]. Based on this evidence, the International Agency for Research on Cancer has concluded that the evidence for the carcinogenicity of technical-grade 1,3-dichloropropene in animals is sufficient [IARC 1986].

2. *Effects on Humans:* Exposure to 1,3-dichloropropene irritates the eyes, skin, and mucous membranes and may produce respiratory damage in humans. Prolonged skin contact with this substance may cause burns or an itching, red rash [NLM 1992]. After an explosion of a tank car containing this substance, exposed workers immediately experienced coughing and choking, followed by headache, dizziness, irritation of the mucous membranes, and chest discomfort; three of the exposed workers lost consciousness and subsequently died. Pulmonary effects included atelectasis, emphysema, pneumonia, and pulmonary edema [Gosselin et al. 1984]. Individuals exposed to 1,3-dichloropropene during a spill reported headache, fatigue, irritation of the mucous membranes, chest pain, and abdominal discomfort that persisted for up to 2 weeks [Gosselin et al. 1984]. Two firemen previously treated for acute symptoms after exposure to 1,3-dichloropropene subsequently developed malignant histiocytic lymphomas [IARC 1986].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 1,3-dichloropropene include pain, redness, and tearing of the eyes; redness and inflammation of the eyelids; redness, burns, and rashes of the skin; headache; fatigue; loss of consciousness; coughing; shortness of breath; chest discomfort; abdominal discomfort; and vomiting. In addition, two cases of malignant histiocytic lymphoma have been reported in workers acutely overexposed to this substance.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to 1,3-dichloropropene include skin burns and cracked, rough, and reddened 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 from exposure to concentrated solutions, vapors, mists, or aerosols of 1,3-dichloropropene! ***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 1,3-dichloropropene 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 1,3-dichloropropene and lead to worker exposures to this substance:

—Use as a soil fumigant

—Use as a chemical intermediate

The following methods are effective in controlling worker exposures to 1,3-dichloropropene, 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.

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 1,3-dichloropropene, 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 1,3-dichloropropene 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 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 1,3-dichloropropene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 1,3-dichloropropene 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 1,3-dichloropropene.

- **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 1,3-dichloropropene is made using a charcoal 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 5 liters is collected. The sample is then treated with carbon disulfide to extract the 1,3-dichloropropene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in NIOSH Method No. 1003 in the *NIOSH Analytical Methods Manual* [NIOSH 1984], which has been modified for use by OSHA.

PERSONAL HYGIENE

1,3-Dichloropropene can be absorbed through the skin in toxic amounts. Therefore, if 1,3-dichloropropene contacts

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

Clothing contaminated with 1,3-dichloropropene 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 1,3-dichloropropene, particularly its ability to be absorbed through the skin in toxic amounts.

A worker who handles 1,3-dichloropropene 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 1,3-dichloropropene is handled, processed, or stored.

STORAGE

1,3-Dichloropropene 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 equipment in storage areas must meet requirements for OSHA Class I flammable liquids. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of 1,3-dichloropropene should be protected from physical damage and should be stored separately from oxidizers, aluminum or magnesium compounds, alkaline or corrosive materials, and 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 1,3-dichloropropene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained 1,3-dichloropropene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 1,3-dichloropropene, 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. Use water spray to reduce vapors; do not get water inside the container.
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 1,3-dichloropropene 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**

  1,3-Dichloropropene 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 1,3-dichloropropene is 100 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

(202) 426-2675 or at (800) 424-8802 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency 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 1,3-dichloropropene 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 1,3-dichloropropene 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. 1,3-Dichloropropene 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. U084. This chemical is approved for land disposal as long as the concentration of 1,3-dichloropropene in the waste or treatment residual does not exceed 18 mg/kg. 1,3-Dichloropropene 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 1,3-dichloropropene 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 1,3-dichloropropene. 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 1,3-dichloropropene and may

provide protection for periods greater than 8 hours: polyvinyl alcohol and Viton (fluorocarbon rubber). A material that may withstand permeation for more than 4 but fewer than 8 hours is Teflon (polytetrafluoroethylene). Butyl rubber, natural rubber, neoprene, nitrile rubber, and polyvinyl chloride have demonstrated poor resistance to permeation by 1,3-dichloropropene.

If 1,3-dichloropropene 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 1,3-dichloropropene 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 1,3-dichloropropene. Contact lenses should not be worn when working with this material.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2,2-DICHLOROPROPIONIC ACID

INTRODUCTION

This guideline summarizes pertinent information about 2,2-dichloropropionic 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**

  $C_3H_4Cl_2O_2$

- **Structure**

  $H_3C—CCl_2—COOH$

- **Synonyms**

  Alatex; Basfapon; BH Dalapon; Basinex; Crisapon; Dalapon; Dalapon 85; Ded-Weed; Devipon; a-dichloropropionic acid; Dowpon; Dowpon M; Gramevin; Kenapon; Liropon; Proprop; Radapon; Revenge; Unipon

- **Identifiers**

  1. CAS No.: 75-99-0
  2. RTECS No.: UF0690000
  3. DOT UN: 1760 60
  4. DOT label: Corrosive

- **Appearance and odor**

  2,2-Dichloropropionic acid is a corrosive, colorless liquid with an acrid odor. The commercial herbicide is a white or tan powder from the sodium and/or magnesium salt. The odor threshold for 2,2-dichloropropionic acid is reported to be 2,500 mg/m^3 (416 ppm).

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 142.97
  2. Boiling point (760 mm Hg): 185° to 190°C (365° to 374°F)
  3. Specific gravity (water = 1): 1.4 at 20°C (68°F)
  4. Vapor density: 4.93
  5. Melting point: 174° to 176°C (345.2° to 348.8°F)
  6. Vapor pressure: 10 mm Hg at 40°C (104°F)
  7. Solubility: Very soluble in water, alcohol, and ether.
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame.

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2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as chlorine) may be released in a fire involving 2,2-dichloropropionic acid.

4. Special precautions: 2,2-Dichloropropionic acid is corrosive to iron, aluminum, and copper.

- **Flammability**

The National Fire Protection Association has not issued a fire hazard rating for 2,2-dichloropropionic acid; this substance is not flammable but may burn.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use dry chemical, regular foam, or carbon dioxide to fight fires involving 2,2-dichloropropionic acid. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving 2,2-dichloropropionic acid 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. Containers of 2,2-dichloropropionic 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. 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 a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving 2,2-dichloropropionic acid. Structural firefighters' protective clothing may provide limited protection against fires involving 2,2-dichloropropionic acid.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for 2,2-dichloropropionic acid [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 ppm (6 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for 2,2-dichloropropionic acid [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned 2,2-dichloropropionic acid a threshold limit value (TLV) of 1 ppm (5.8 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 skin, eye, respiratory, and gastrointestinal irritation associated with 2,2-dichloropropionic acid exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to 2,2-dichloropropionic acid can occur through inhalation, ingestion, and eye or skin contact; absorption through the skin is said to be "negligible."

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to 2,2-dichloropropionic acid in liquid or vapor form causes corrosion of the eyes and skin; chronic exposure may cause kidney injury. Applied to the skin of rabbits, the sodium salt of 2,2-dichloropropionic acid caused necrosis, and instillation of this substance into the eyes of rabbits caused reversible conjunctival irritation [ACGIH 1991]. The oral LD_{50} in rats is >5,000 mg/kg [NIOSH 1994]. The oral LD_{50} in rats for sodium 2,2-dichloropropionic acid is 9,330 mg/kg (male) and 7,570 mg/kg (female) [Farm Chemicals Handbook 1994]. Exposure to an atmosphere saturated with 2,2-dichloropropionic acid for 7 hours produced no observable effects in rats [ACGIH 1991]. Rats fed 15 mg/kg/day of this substance for 120 days had no ill effects [ACGIH 1991]. Dogs fed 100 mg/kg/day of 2,2-dichloropropionic acid for 1 year and rats given 50 mg/kg/day for the same period showed increased

kidney weights at autopsy [ACGIH 1991]. Dogs given 50 mg/kg/day for 1 year or rats given 15 mg/kg/day for 2 years, showed no significant changes at autopsy [ACGIH 1991].

2. *Effects on Humans:* Exposure to 2,2-dichloropropionic acid causes irritation of the eyes, respiratory tract, and skin, and contact of the eyes or skin with the liquid or vapor can lead to burns. Repeated or prolonged skin contact may cause dermatitis [NJDH 1989]. Exposure to a 2- to 7 ppm concentration of this substance for an unspecified time produced respiratory irritation described as "minimal" [ACGIH 1991], and systemic poisoning caused by acute exposure to an unspecified concentration of this substance resulted in lassitude, vomiting, diarrhea, slowed pulse, and anorexia [NLM 1994].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to 2,2-dichloropropionic acid include redness and inflammation of the eyes and eyelids, runny nose, sore throat, coughing, sneezing, difficulty breathing, and reddened and cracked skin. Lassitude, anorexia, vomiting, and diarrhea have also been reported. In contact with the eyes or skin, the vapor or liquid of this substance may cause eye or skin burns.

2. *Chronic exposure:* The signs and symptoms of repeated or prolonged skin exposure to 2,2-dichloropropionic acid include reddened, cracked, and blistered skin. Long-term high exposure to 2,2-dichloropropionic acid may affect the liver and kidneys.

- **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 2,2-dichloropropionic 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, 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. *Ingestion exposure:* Take the following steps if 2,2-dichloropropionic acid 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, 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 2,2-dichloropropionic acid and lead to worker exposures to this substance:

—Use as a herbicide

The following methods are effective in controlling worker exposures to 2,2-dichloropropionic acid, 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 2,2-dichloropropionic 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 respiratory system, skin, liver, and kidneys. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society (ATS) [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 2,2-dichloropropionic acid 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 of skin allergies or findings consistent with diseases of the respiratory system, skin, 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 2,2-dichloropropionic acid exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of 2,2-dichloropropionic acid on the

respiratory system, skin, 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 2,2-dichloropropionic 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 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 2,2-dichloropropionic acid is made using a silica gel tube (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 10 liters is collected. The sample is then treated with deionized water to extract the 2,2-dichloropropionic acid. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1993].

PERSONAL HYGIENE

2,2-Dichloropropionic acid is corrosive; therefore, if this substance 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 2,2-dichloropropionic acid 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 2,2-dichloropropionic acid, particularly its potential to cause burns of the skin on contact.

A worker who handles 2,2-dichloropropionic acid 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 2,2-dichloropropionic acid or a solution containing 2,2-dichloropropionic acid is handled, processed, or stored.

STORAGE

2,2-Dichloropropionic 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 2,2-dichloropropionic acid should be protected from physical damage and should be stored separately from aluminum and ferric compounds. Because containers that formerly contained 2,2-dichloropropionic acid may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving 2,2-dichloropropionic acid, 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 the area of the spill or leak.
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, 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 2,2-dichloropropionic 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**

  2,2-Dichloropropionic 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 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 2,2-dichloropropionic 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 2,2-dichloropropionic 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 2,2-dichloropropionic 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 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 2,2-dichloropropionic 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 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 gloves and clothing should be worn to prevent any skin contact with 2,2-dichloropropionic 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. No reports have been published on the resistance of various protective clothing materials to 2,2-dichloropropionic 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 2,2-dichloropropionic acid.

If 2,2-dichloropropionic 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 2,2-dichloropropionic 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 2,2-dichloropropionic acid. Contact lenses should not be worn if the potential exists for 2,2-dichloropropionic acid exposure.

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Occupational Health Guideline for Dichlorotetrafluoroethane (Refrigerant 114)

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: $F_2ClCCClF_2$
- Synonyms: 1,2-Dichlorotetrafluoroethane; Freon 114; Refrigerant 114; Halon 242
- Appearance and odor: Colorless liquid or gas with a very slight ethereal odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Refrigerant 114 is 1000 parts of Refrigerant 114 per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 7000 milligrams of Refrigerant 114 per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Refrigerant 114 can affect the body if it is inhaled or if the liquid 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: Breathing in very high concentrations may cause drowsiness and unconsciousness and may also cause the heart to beat irregularly or to stop suddenly. If the liquid gets on the skin or in the eyes, it may cause frostbite.

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 Refrigerant 114.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Refrigerant 114 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 Refrigerant 114 exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Refrigerant 114 might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of Refrigerant 114 might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Refrigerant 114 vapor is a respiratory irritant and causes asphyxia at extremely high concentrations. Exposure to 200,000 ppm for 16 hours was fatal to dogs, while single 8-hour exposures produced tremors and convulsions but no fatalities; repeated exposures at 140,000 to 160,000 ppm for 8 hours caused incoordination, tremors, and occasionally convulsions, but all dogs survived. At 47,000 ppm guinea pigs developed respiratory irritation. Sniffing aerosols of fluorochlorinated hydrocarbons has caused sudden death by cardiac arrest, probably due to sensitization of the myocardium. The liquid spilled on the skin may produce frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 170.9
  2. Boiling point (760 mm Hg): 3.5 C (38.4 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.

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

3. Specific gravity (water = 1): 1.44
4. Vapor density (air = 1 at boiling point of Refrigerant 114): 5.9
5. Melting point: −94 C (−137 F)
6. Vapor pressure at 20 C (68 F): 1444 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.01
8. Evaporation rate (butyl acetate = 1): Higher than 1

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Refrigerant 114 reacts with chemically active metals such as sodium. potassium, calcium, powdered aluminum, zinc, and magnesium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and hydrogen fluoride) may be released when Refrigerant 114 decomposes.
4. Special precautions: Liquid Refrigerant 114 will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Although Refrigerant 114 has a chloroform-like odor, no quantitative data are available relating warning properties to air concentrations. It is treated, therefore, as a material with poor warning properties.
Refrigerant 114 is not a known 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 Refrigerant 114 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 the skin from becoming wet with liquid Refrigerant 114.

• Any clothing which becomes wet with liquid Refrigerant 114 should be removed immediately and not reworn until the Refrigerant 114 has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid Refrigerant 114 may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Refrigerant 114 may occur and control methods which may be effective in each case:

Operation	Controls
Manufacture and use in aerosols with other Freons to lower vapor pressure and produce non-flammable aerosol propellants; use as a refrigerant in industrial cooling and airconditioning systems	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a blowing agent for cellular polymers; use as a solvent and diluent in polymerization of fluoro-olefins, cleaning and degreasing printed circuit boards, preparation of explosives, and extraction of volatile substances	General dilution ventilation; local exhaust ventilation; personal protective equipment

Use as a foaming agent in fire extinguishing and aerosols; in organic synthesis in preparation of uranium tetrafluoride, Freons, and polymer intermediates	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in inhibiting of metal erosion in hydraulic fluids; in strengthening glass bottles; in magnesium refining; and as a reflux liquid to assist heat removal	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 Refrigerant 114 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 liquid Refrigerant 114 gets on the skin, immediately flush the contaminated skin with water if the Refrigerant 114 has not already evaporated. If liquid Refrigerant 114 soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of Refrigerant 114, 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 Refrigerant 114 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 until cleanup has been completed.

• If Refrigerant 114 is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If the gas is leaking, stop the flow.
3. If the liquid is spilled or leaked, allow to vaporize.

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RESPIRATORY PROTECTION FOR REFRIGERANT 114

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Gas Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50,000 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 with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
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 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 Dichlorvos

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: $(CH_3O)_2POOCH=CCl_2$ or $C_4H_7Cl_2O_4P$
- Synonyms: DDVP; 2,2-dichlorovinyl dimethyl phosphate
- Appearance and odor: Colorless to amber liquid with a mild chemical odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dichlorvos is 1 milligram of dichlorvos per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dichlorvos 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 dichlorvos, 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 dichlorvos, 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 dichlorvos may make a person more susceptible to the effects of this and related chemicals. Repeated exposure 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 dichlorvos.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dichlorvos 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 disorders.

—Cholinesterase determination: Dichlorvos (DDVP) causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity 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 determi-

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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nation which should be performed quarterly or at any time overexposure is suspected or signs and symptoms of toxicity occur.

• **Summary of toxicology**

Dichlorvos (DDVP) is an anticholinesterase agent; absorption may occur from inhalation of the vapor or mist, from skin absorption of the liquid, or from ingestion. 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. In a study of 13 workers exposed for 12 months to an average concentration of 0.7 mg/m^3, the erythrocyte cholinesterase activity was reduced by approximately 35%, and the serum cholinesterase activity was reduced by 60%; the results of other tests and of thorough medical examinations conducted at regular intervals were entirely normal.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 221
2. Boiling point (1 mm Hg): 77 C (170 F)
3. Specific gravity (water = 1): 1.44
4. Vapor density (air = 1 at boiling point of dichlorvos): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 32 C (90 F): 0.032 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1 (approx).
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 gas, phosphoric acid mist, and carbon monoxide) may be released in a fire involving dichlorvos.
4. Special precautions: Dichlorvos will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of dichlorvos.
2. Eye Irritation Level: Dichlorvos 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 dichlorvos, it is treated as a material with poor warning properties. The concentration in saturated air at 20 C could result in a significant exposure relative to the permissible 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**

An analytical method for dichlorvos 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 dichlorvos.
- Clothing contaminated with dichlorvos should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dichlorvos from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dichlorvos, the person performing the operation should be informed of dichlorvos's hazardous properties.
- Non-impervious clothing which becomes contaminated with dichlorvos should be removed immediately and not reworn until the dichlorvos is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid dichlorvos may contact the eyes.

SANITATION

- Skin that becomes contaminated with dichlorvos should be immediately washed or showered with soap or mild detergent and water to remove any dichlorvos.
- Employees who handle dichlorvos 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 dichlorvos may occur and control methods which may be effective in each case:

Operation	Controls
Formulation and mixing for insecticidal application	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Application on vegetables, animals, agriculutral premises, and for outdoor fogging; insecticidal use of tablets, rubbing devices, resin strips, animal collars, dust on animals, animal buildings, restaurants, hospitals, and aircraft	Personal protective equipment
Manufacture of dichlorvos	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 dichlorvos or dichlorvos 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 dichlorvos or dichlorvos mists get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If dichlorvos or dichlorvos mists soak 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 dichlorvos, 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 dichlorvos 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. Under-

stand 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 dichlorvos 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:

Dichlorvos may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR DICHLORVOS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate or Vapor Concentration	
10 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ or less	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.
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.
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 dichlorvos; 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 SAFETY AND HEALTH GUIDELINE FOR DICROTOPHOS

INTRODUCTION

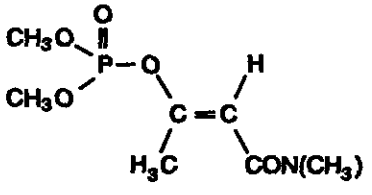
This guideline summarizes pertinent information about dicrotophos for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations 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**

$C_8H_{16}NO_5P$

- **Structure**



- **Synonyms**

Bidrin; phosphoric acid, dimethyl ester; ester with (E)-3-hydroxy-N,N-dimethylcrotonamide; Bidirl; Carbicron; Ektafos; Oleobidrin; 3-(dimethylamino)-1-methyl-3-oxo-1-propenyl dimethyl phosphate (E)-isomer; dimethyl 1-dimethylcarbonyl-1-propen-2-yl phosphate

- **Identifiers**

1. CAS No.: 141-66-2
2. RTECS No.: TC3850000
3. DOT NA: 2783 55
4. DOT label: Poison

- **Appearance and odor**

Dicrotophos is a yellow-brown liquid with a mild ester odor. Eighty-five percent of the commercial grade consists of the E-isomer, which is amber in color and more insecticidally active than the Z-isomer.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 237.21
2. Boiling point (760 mm Hg): 400°C (752°F)
3. Specific gravity (water = 1): 1.22 at 15°C (59°F)
4. Vapor density: Data not available
5. Melting point: Data not available
6. Vapor pressure at 20°C (68°F): 0.0001 mm Hg
7. Solubility: Miscible with water, methylene chloride, ethanol, isopropyl and diacetone alcohols, acetoni-

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trile, and xylene; slightly soluble in kerosene and diesel fuel.

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 (such as oxides of phosphorus and nitrogen) may be released in a fire involving dicrotophos.

4. Special precautions: Dicrotophos is somewhat corrosive to cast iron, mild steel, brass, and stainless steel 304.

Flammability

The National Fire Protection Association has not assigned a fire hazard rating to dicrotophos.

1. Flash point: Greater than 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 standard foam to fight fires involving dicrotophos.

Fires involving dicrotophos 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 dicrotophos 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 dicrotophos. Chemical protective clothing that is specifically recommended for dicrotophos may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving dicrotophos.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dicrotophos [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 0.25 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for dicrotophos. 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 dicrotophos a threshold limit value (TLV) of 0.25 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned a "Skin" notation to dicrotophos [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to dicrotophos.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to dicrotophos can occur through inhalation, ingestion, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Dicrotophos is a highly toxic organophosphorus pesticide that causes cholinesterase inhibition in animals [EPA 1989]. The dermal LD_{50} in rabbits is 168 mg/kg [NIOSH 1993]. The 4-hr LC_{50} in rats is 90 mg/m^3 [NIOSH 1993]. The oral LD_{50} is 13 mg/kg in rats and 11 mg/kg in mice [NIOSH 1993]. Rats fed dicrotophos for 2 years at a dietary level of 1, 10, or 100 ppm showed no effects at the 1-ppm level

but had decreased body weights and reduced cholinesterase activity at the higher levels [ACGIH 1991]. Dogs fed 0.16, 1.6, or 16 ppm for 2 years experienced mild episodes of excessive salivation and, at the highest dose, showed depressed plasma and red blood cell cholinesterase activity [ACGIH 1991].

2. *Effects on Humans:* Dicrotophos is an inhibitor of plasma and red blood cell cholinesterase activity in humans. There are two reports of severe poisoning attributed to dicrotophos, one involving a 41-year-old farmer who had applied this substance to his crops and used it inside his house to control insects, and the other involving a 52-year-old man who ingested a mixture of turpentine and dicrotophos after a drinking bout [Hayes 1982]. Both of these patients eventually recovered after initially responding to treatment and then relapsing seriously [Hayes 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dicrotophos include those of cholinesterase inhibition: headache, nausea, dizziness, anxiety, restlessness, muscle twitching, weakness, tremor, incoordination, vomiting, abdominal cramps, and diarrhea; excessive salivation, sweating, tearing of the eyes, and runny nose also may occur.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to dicrotophos include persistent anorexia, weakness, and malaise, brought on by repeated absorption of dicrotophos in amounts that are not sufficient to cause acute poisoning.

- **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*** rinse concentrated solutions, vapors, mists, or aerosols of dicrotophos from 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 concentrated solutions, vapors, mists, or aerosols of dicrotophos. Dicrotophos 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 vapors, mists, or aerosols of dicrotophos 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 dicrotophos 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 dicrotophos and lead to worker exposures to this substance:

—Manufacture, formulation, and application of dicrotophos-containing insecticides and acaricides to cotton, apples, grains, vegetables, ornamentals, shrubs, trees, and other crops

The following methods that are effective in controlling worker exposures to dicrotophos, 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.

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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 dicrotophos, 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 blood. A pre-exposure red blood cell and plasma 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 dicrotophos 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.

- **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 dicrotophos exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicrotophos on red blood cell and plasma 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 red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophorus compounds such as dicrotophos. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for dicrotophos (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70 percent 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 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 a patient who has recovered from the acute phase of organophosphorus poisoning remains hypersusceptible to anticholinesterases for as long as several weeks or months, the need for medical monitoring may extend well beyond the acute poisoning episode.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicrotophos is made 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 maximum air volume of 480 liters is collected. The sample is then treated with toluene to extract the dicrotophos. Analysis is conducted by gas chromatography using a flame photometric detector. This method is included in the OSHA Laboratory In-House Methods File [1989].

PERSONAL HYGIENE

Dicrotophos can be absorbed through the skin in toxic amounts. Therefore, if dicrotophos contacts the skin, workers should immediately and repeatedly wash the body (including hair, scalp, and nails) with soap and water. Get medical help immediately.

Clothing contaminated with dicrotophos 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 dicrotophos, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles dicrotophos 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 dicrotophos or a solution containing dicrotophos is handled, processed, or stored.

STORAGE

Dicrotophos 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 located at a suitable distance from inhabited buildings, animal shelters, and food stores and must be inaccessible to unauthorized persons. Containers of dicrotophos should be protected from physical damage, heat, sparks, and open flame. Dicrotophos decomposes when stored at temperatures about 25°C to 30°C (77°F to 86°F). Containers should be stacked in a manner that permits free circulation of air at the bottom and insides of the stacks of containers.

SPILLS AND LEAKS

In the event of a spill or leak involving dicrotophos, 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; do not get water inside the container.

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 dicrotophos 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 100 lb or more of dicrotophos must comply with EPA's emergency planning requirements [40 CFR 355.40].

- **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 dicrotophos 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 State 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 dicrotophos 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 dicrotophos 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 dicrotophos 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, full-body covering, and head protection) should be worn as appropriate to prevent any possibility of skin contact with dicrotophos. 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 dicrotophos permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have shown that material made of a laminate of Vitron/neoprene or butyl rubber/neoprene provides good protection against permeation by this group of substances. Since specific test data are not available for dicrotophos, 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 dicrotophos.

If dicrotophos 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 dicrotophos 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 dicrotophos.

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 DICYCLOPENTADIENE

INTRODUCTION

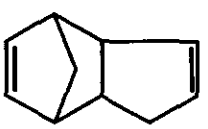
This guideline summarizes pertinent information about dicyclopentadiene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations 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**

  $C_{10}H_{12}$

- **Structure**



- **Synonyms**

  1,3-Cyclopentadiene, dimer; alpha-dicyclopentadiene (endo form); bicyclopentadiene; biscyclopentadiene; cyclopentadiene dimer; 3a,4,7,7a-tetrahydro-4,7-methanoindene

- **Identifiers**

  1. CAS No.: 77-73-6
  2. RTECS No.: PC1050000
  3. DOT UN: 2048 26
  4. DOT label: Flammable liquid (or solid)

- **Appearance and odor**

  Dicyclopentadiene is a flammable tricyclic compound that exists either as a solid or a clear liquid, depending on temperature. In the solid state, dicyclopentadiene is a colorless, combustible crystalline substance that has a disagreeable camphor-like odor. Dicyclopentadiene exists in two stereoisomeric forms, the endo and exo isomers; the commercial product consists predominantly of the endo isomer. The odor is detectable below 0.2 ppm, but does not become noticeably irritating below 10 ppm.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 132.21
  2. Boiling point (760 mm Hg): 172°C (342°F); depolymerizes at boiling point to form two molecules of cyclopentadiene.

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. Specific gravity (water = 1): 0.98 at 35°C (95°F)

4. Vapor density (air = 1 at boiling point of dicyclopentadiene): 4.6

5. Melting point: 32°C (89.6°F)

6. Vapor pressure at 20°C (68°F): 1.4 mm Hg

7. Solubility: Insoluble in water; soluble in acetic acid and alcohol; very soluble in ether and carbon tetrachloride.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of dicyclopentadiene with oxidizing agents can cause fires and explosions.

3. Hazardous decomposition products: Thermal-oxidative degradation products can include cyclopentadiene and partial oxidation products of carbon monoxide and carbon dioxide. When heated to decomposition, dicyclopentadiene emits acrid smoke and fumes.

4. Special precautions: Dicyclopentadiene must be inhibited and maintained under an inert atmosphere to prevent hazardous polymerization. In contact with air, especially when heated, dicyclopentadiene forms peroxides; the level of these can be controlled by the addition of an inhibitor.

Flammability

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

1. Flash point: 32°C (90°F) (open cup)

2. Autoignition temperature: 503°C (937°F)

3. Flammable limits in air: Lower, 0.8; upper, 6.3

4. Extinguishant: Use dry chemical, carbon dioxide, alcohol-resistant foam, or water fog to fight fires involving dicyclopentadiene.

Fires involving dicyclopentadiene 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 dicyclopentadiene 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 a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicyclopentadiene. Structural firefighters' protective clothing may provide limited protection against fires involving dicyclopentadiene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dicyclopentadiene [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 (30 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for dicyclopentadiene [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicyclopentadiene a threshold limit value (TLV) of 5 ppm (27 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 skin irritation associated with dicyclopentadiene exposure. The ACGIH limit is based on the risk of irritation, kidney damage, and pulmonary effects associated with exposure to dicyclopentadiene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Dicyclopentadiene is an irritant of the eyes and skin and a narcotic on acute exposure; chronic exposure causes kidney and lung damage. Applied to the skin of rabbits, dicyclopentadiene causes moderate to severe irritation; instilled into the rabbit eye, this substance causes mild and reversible irritation [NIOSH 1993; Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is 5,080 mg/kg [NIOSH 1993]. The 4-hr LC_{50} is 145 ppm in mice and 372 ppm in rats [NIOSH 1993; Sax and Lewis 1989]. The oral LD_{50} is 353 mg/kg in rats and 190 mg/kg in mice [NIOSH 1993]. Acutely poisoned animals showed signs of eye irritation, lost coordination, and convulsed before death [ACGIH 1991]. Rats exposed daily for 10 days to dicyclopentadiene concentrations of 72 or 146 ppm survived, but rats exposed on the same regimen to a concentration of 332 ppm died [ACGIH 1991]. Rats exposed to a 35- or 74-ppm concentration of dicyclopentadiene for 7 hours/day for 89 days showed, at autopsy, kidney damage and some lung involvement [ACGIH 1991]. Leukocytosis was found in rats 96-hr post-subcutaneous administration of dicyclopentadiene [Clayton and Clayton 1981; NLM 1992].

2. *Effects on Humans:* Dicyclopentadiene is an irritant of the eyes, nose, throat, and skin in humans [NJDH 1989]. Exposed workers also experience headaches and other central nervous system effects [NLM 1992]. Workers exposed accidentally to a high but unspecified concentration of dicyclopentadiene experienced headaches for the first two months after exposure but did not continue to experience this symptom indicating a certain degree of inurement [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dicyclopentadiene include redness, tearing, and inflammation of the eyes, sneezing, and coughing. Contact of the skin with this substance causes redness and may cause blistering. Headaches and loss of coordination also may occur after an acute overexposure.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to dicyclopentadiene may include those associated with kidney damage, such as blood, pus, or protein in the urine, or with lung damage, such as difficult breathing, rales, and fluid in the lungs.

- **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 dicyclopentadiene. ***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:* Irritation 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 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 dicyclopentadiene 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 dicyclopentadiene and lead to worker exposures to this substance:

—Use as a chemical intermediate during chlorinated hydrocarbon pesticide synthesis and to stabilize organophosphorus insecticides

—Use in the production of ferrocene and other metallocene compounds

—Use as an intermediate in the production of plasticizers, elastomers, pharmaceuticals, resins, paints, varnishes, paint driers, and perfumes

—Use as a polyhalogenated flame retardant for plastics

The following methods are effective in controlling worker exposures to dicyclopentadiene, 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.

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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 dicyclopentadiene, 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 eyes, skin, 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 detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is

exposed to dicyclopentadiene 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 eyes, skin, kidneys, 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 dicyclopentadiene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicyclopentadiene on the eyes, skin, kidneys, 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 dicyclopentadiene.

- **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 dicyclopentadiene is made using a charcoal tube (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 dicyclopentadiene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is abstracted in the *OSHA Chemical Information Manual* [OSHA 1987] and can be found in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

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

Clothing contaminated with dicyclopentadiene 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 dicyclopentadiene, particularly its potential to cause skin irritation.

A worker who handles dicyclopentadiene 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 dicyclopentadiene or a solution containing dicyclopentadiene is handled, processed, or stored.

STORAGE

Dicyclopentadiene should be stored in a cool, dry, well-ventilated area in tightly sealed, stainless steel containers that are maintained under an inert blanket and are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet requirements for an OSHA Class IB flammable liquid. Only explosion-proof ventilation may be used. Containers of dicyclopentadiene 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 dicyclopentadiene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dicyclopentadiene, 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. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. Use non-sparking tools 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.
8. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
9. For large liquid spills, build dikes far ahead of the spill to contain the dicyclopentadiene for later reclamation or disposal.

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**

  Dicyclopentadiene 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 dicyclopentadiene; 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 dicyclopentadiene 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 dicyclopentadiene 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 dicyclopentadiene 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* [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 dicyclopentadiene. 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 dicyclopentadiene 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 dicyclopentadiene.

If dicyclopentadiene 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 dicyclopentadiene 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 dicyclopentadiene. Contact lenses should not be worn if the potential exists for dicyclopentadiene exposure.

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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 DICYCLOPENTADIENYL IRON

INTRODUCTION

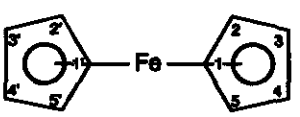
This guideline summarizes pertinent information about dicyclopentadienyl iron for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. 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**

  $(C_5H_5)_2Fe$

- **Structure**



- **Synonyms**

  Ferrotsen; ferrocene; biscyclopentadienyl iron; di-2,4-cyclopentadien-1-yl iron; iron bis(cyclopentadiene); iron bis(cyclopentadienide); iron dicyclopentadienyl; bis(eta(5)-2,4-cyclopentadien-1-yl)-iron

- **Identifiers**

  1. CAS No.: 102-54-5
  2. RTECS No.: LK0700000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Dicyclopentadienyl iron is a flammable, bright orange, crystalline solid with a camphor-like odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 186.05
  2. Boiling point (760 mm Hg): 249°C (408.2°F) (sublimes above 100°C (212°F))
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: 173°-174°C (343°-345°F)
  6. Vapor pressure at 20°C (68°F): Data not available
  7. Solubility: Insoluble in water; soluble in alcohol, ether, and benzene
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, and steam
  2. Incompatibilities: Contact of dicyclopentadienyl iron

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with tetranitromethane may lead to violent explosions. This substance also reacts violently with ammonium perchlorate and mercury (II) nitrate.

3. Hazardous decomposition products: Thermal oxidative decomposition of dicyclopentadienyl iron can produce acrid smoke and irritating fumes.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to dicyclopentadienyl iron. Other sources rate dicyclopentadienyl iron as a moderate fire risk.

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 proper extinguishant for fires involving dicyclopentadienyl iron.

Fires involving dicyclopentadienyl iron 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 dicyclopentadienyl iron may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicyclopentadienyl iron.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for dicyclopentadienyl iron 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 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 dicyclopentadienyl iron 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 NIOSH limits are based on the risk of mutagenicity associated with exposure to dicyclopentadienyl iron [54 Fed. Reg. 2592; NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to dicyclopentadienyl iron may cause liver, red blood cell, and testicular changes in experimental animals. The LC_{50} for an unspecified period of time in rats is greater than 150 mg/m^3 [Hathaway et al. 1991]. The oral LD_{50} is 1,320 mg/kg in rats and 832 mg/kg in mice [NIOSH 1993]. Ten 200 mg/kg oral doses of dicyclopentadienyl iron administered over a 2-week period caused no fatalities in rats [Hathaway et al. 1991]. In a 6-month subchronic study in dogs, oral doses of 30 to 300 mg/kg/day dicyclopentadienyl iron caused hemosiderosis (iron deposits) in the liver [Hathaway et al. 1991; ACGIH 1991]. Dogs exposed to a 300-mg/kg/day dose of dicyclopentadienyl iron for an unspecified period of time developed cirrhosis of the liver; reversible decreases in hemoglobin, packed red cell volume, and red cell count were also seen in these animals within the first 4 weeks of exposure on this regimen [Hathaway et al. 1991]. Testicular hypoplasia developed in dogs given oral dicyclopentadienyl iron doses of 100 mg/kg/day for 6 months [Hathaway et al. 1991; ACGIH 1991]. Dicyclopentadienyl iron is mutagenic in mouse lymphoma test systems [NLM 1992].

2. *Effects on Humans:* No data are available on the

effects of exposure to dicyclopentadienyl iron in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to dicyclopentadienyl iron have been reported in humans.

2. *Chronic exposure:* Based on effects seen in animals, chronic exposure to dicyclopentadienyl iron may cause liver, red blood cell, or testicular damage.

- **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 dicyclopentadienyl iron 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 dicyclopentadienyl iron and lead to worker exposures to this substance:

—Use as an additive in oil and gasoline fuel to improve efficiency of combustion and eliminate smoke

—Manufacture of rubber, silicone resins, and high-temperature polymers

—Use as coating for missiles and satellites

—Use as a combustion catalyst

The following methods are effective in controlling worker exposures to dicyclopentadienyl iron, 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 dicyclopentadienyl iron, 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 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 dicyclopentadienyl iron 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 blood 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 dicyclopentadienyl iron exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicyclopentadienyl iron on the blood 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. No biological monitoring test acceptable for routine use has yet been developed for dicyclopentadienyl iron.

- **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 dicyclopentadienyl iron is made using a mixed cellulose ester filter (MCEF) with a 0.8-micron pore size. 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 atomic absorption spectroscopy (or by inductively coupled argon plasma atomic emission spectroscopy). This method has a sampling and analytical error of 0.16 and is described in OSHA Methods No. ID-121 and No. ID-125G in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

If dicyclopentadienyl iron 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 dicyclopentadienyl iron 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 dicyclopentadienyl iron.

A worker who handles dicyclopentadienyl iron 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 dicyclopentadienyl iron is handled, processed, or stored.

STORAGE

Dicyclopentadienyl iron 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 dicyclopentadienyl iron should be protected from physical damage and should be stored separately from ammonium perchlorate, tetranitromethane, mercury (II) nitrate, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dicyclopentadienyl iron may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dicyclopentadienyl iron, 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 the area of the spill or leak.
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, take up with activated carbon 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 dicyclopentadienyl iron 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**

  Dicyclopentadienyl iron 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 dicyclopentadienyl iron; 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 dicyclopentadienyl iron 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 dicyclopentadienyl iron 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 dicyclopentadienyl iron 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 (gloves, boots, aprons, and gauntlets, as necessary) should be worn to prevent skin contact with dicyclopentadienyl iron. 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 dicyclopentadienyl iron 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 dicyclopentadienyl iron.

If dicyclopentadienyl iron 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 dicyclopentadienyl iron 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 dicyclopentadienyl iron. Contact lenses should not be worn if the potential exists for dicyclopentadienyl iron 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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CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

54 Fed. Reg. 2592 [1989]. Occupational Safety and Health Administration. 29 CFR Part 1910: air contaminants; final rule. Washington, DC: U.S. Government Printing Office.

Hathaway GJ, Proctor NH, Hughes JP, and Fischman, ML [1991]. Proctor and Hughes' chemical hazards of the workplace. 3rd ed. New York, NY: Van Nostrand Reinhold.

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OSHA [1992]. Computerized information system. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIELDRIN

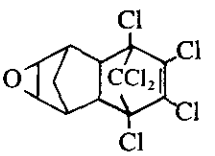
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about dieldrin 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:** $C_{12}H_8Cl_6O$
- **Structure:**



- **Synonyms:** Dieldrex; dieldrine; 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro,endo,exo-1,4:5,8-dimethanonaphthalene; illoxol; octalox
- **Identifiers:** CAS 60-57-1; RTECS IO1750000; DOT 2761
- **Appearance and odor:** Light brown crystals with a mild chemical odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 380.90
2. Boiling point (at 760 mmHg): Decomposes
3. Specific gravity (water = 1): 1.75
4. Vapor density (air = 1 at boiling point of dieldrin): 13.2
5. Melting point: 176°C (349°F)
6. Vapor pressure at 20°C (68°F): 1.8×10^{-7} mmHg
7. Solubility in water, mg/l water at 25°-29°C (77°-84°F): 0.186

- **Reactivity**

1. Incompatibilities: Dieldrin 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 dieldrin.
3. Caution: Dieldrin should be stored in a tightly closed container in a well-ventilated area.

- **Flammability**

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 dieldrin is 0.25 milligrams of dieldrin 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 the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that dieldrin be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limt. The NIOSH recommended exposure limit (REL) is 0.15 mg/m^3 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 0.25 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 dieldrin

	Exposure limits mg/m^3
OSHA PEL TWA (Skin)*	0.25
NIOSH REL TWA (Ca)†	0.15§
ACGIH TLV® (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.

NOTE: Most uses of dieldrin were suspended by the Environmental Protection Agency, effective October 18, 1974. The only

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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.

HEALTH HAZARD

• Routes of exposure

Dieldrin may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact. Dermal absorption is substantially increased when dieldrin is dissolved in organic solvents.

• Summary of toxicology

1. *Effects on animals:* Acute oral administration of dieldrin to rats caused liver and kidney degeneration. Chronic oral administration of dieldrin produced enlarged livers and increased liver enzyme activities in mice and rats, liver and lung cancers in mice, and adrenal cancer in rats. Dieldrin fed to pregnant mice and hamsters caused increased fetal deaths, congenital anomalies, and growth retardation in the offspring.
2. *Effects on humans:* Dieldrin is a neurotoxin and may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to dieldrin can cause hyperirritability, headache, dizziness, nausea, vomiting, blood in the urine, tremors, convulsions, and coma.
2. *Long-term (chronic):* Exposure to dieldrin can cause 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 dieldrin, 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 skin, eyes, liver, kidneys, 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 dieldrin 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, and hematopoietic and reproductive systems. Workers should inform their physicians of their potential for exposures to dieldrin 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 a 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 dieldrin. 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 eyes, skin, liver, kidneys, 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 dieldrin 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 dieldrin 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 dieldrin with glass fiber filters followed by extraction with isooctane and analysis by gas chromatography. A detailed sampling and analytical method for dieldrin may be found in the *NIOSH Manual of Analytical Methods* (method number S283).

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 dieldrin.

SANITATION

Clothing which is contaminated with dieldrin 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 dieldrin from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of dieldrin'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 dieldrin 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 dieldrin 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 dieldrin 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 dieldrin

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 dieldrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

If dieldrin 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 dieldrin, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If dieldrin gets on the skin, wash it immediately with soap and water. If dieldrin 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 dieldrin is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Dieldrin solid may be collected and placed in an appropriate container.
3. Dieldrin dust may be collected by vacuuming with an appropriate high-efficiency filtration system.
4. For small quantities of liquids containing dieldrin, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing dieldrin 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 dieldrin

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 DIETHANOLAMINE

INTRODUCTION

This guideline summarizes pertinent information about diethanolamine 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**

  $C_4H_{11}NO_2$

- **Structure**

  $HO(CH_2)_2NH(CH_2)_2OH$

- **Synonyms**

  N,N-Diethanolamine; iminodiethanol; diolamine; diethylolamine; 2,2'-dihydroxydiethylamine; DEA; bis(2-hydroxyethyl)amine; 2,2'iminobisethanol

- **Identifiers**

  1. CAS No.: 111-42-2
  2. RTECS No.: KL2975000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Diethanolamine is a combustible substance that can exist in the form of colorless crystals or a viscous liquid at room temperature. It has a mild, ammonia-like odor and is usually found in liquid form.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 105.14
  2. Boiling point (760 mm Hg): 269°C (516.2°F) (decomposes)
  3. Specific gravity (water = 1): 1.09 at 30°C (86°F)
  4. Vapor density (air = 1 at boiling point of diethanolamine): 3.65
  5. Melting point: 28°C (82.4°F)
  6. Vapor pressure at 20°C (68°F): Less than or equal to 0.01 mm Hg
  7. Solubility: Very soluble in water and alcohol; insoluble in ether and benzene; miscible with acetone and methanol.

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 (ether = 1): Greater than 5,000

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame. Diethanolamine reacts with carbon dioxide in the air.

2. Incompatibilities: Contact of diethanolamine with oxidizing agents or acidic materials can cause fires or explosions.

3. Hazardous decomposition products: Toxic gases (such as carbon monoxide, carbon dioxide, and oxides of nitrogen) may be released in a fire involving diethanolamine.

4. Special precautions: Diethanolamine is corrosive to copper, copper alloys, zinc, and galvanized iron.

Flammability

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethanolamine.

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

2. Autoignition temperature: 661.5°C (1,224°F)

3. Flammable limits in air (% by volume): Lower, 1.6; upper, 9.8

4. Extinguishant: Use dry chemical, carbon dioxide, alcohol foam, or water spray. A solid stream of water or foam directed into burning liquid diethanolamine may cause frothing. Use water spray to cool fire-exposed containers and to dilute liquid to a less flammable solution.

Fires involving diethanolamine 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 diethanolamine.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diethanolamine [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 3 ppm (15 mg/m^3) as a TWA for up to 10-hr workday and a 40-hr workweek for diethanolamine [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diethanolamine a threshold limit value (TLV) of 3 ppm (13 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 and skin irritation associated with exposure to diethanolamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Diethanolamine is an irritant of the eyes and skin and, when administered orally or intraperitoneally, a kidney and liver toxin in animals. Applied to rabbit skin in a 10-percent solution, diethanolamine caused redness, and the application of more concentrated solutions caused a greater degree of injury [Clayton and Clayton 1981]. Instillation of the undiluted liquid or a 40-percent solution into rabbit eyes caused severe burns; whereas, 15 percent solution produces only minor damage [Clayton and Clayton 1981]. The dermal LD_{50} in rabbits is 12.2 g/kg [NIOSH 1993]. The oral LD_{50} is 710 mg/kg in rats, 3,300 mg/kg in mice, and 2,200 mg/kg in rabbits [NIOSH 1993]. Animals given large intraperitoneal doses lose the righting reflex, become uncoordinated and cyanotic, and die [Gosselin et al. 1984]. Rats administered 100 or 500 mg/kg

diethanolamine intraperitoneally were autopsied 4 or 24 hours after dosing and showed cytoplasmic vacuolization of the liver and kidneys and, at the higher dose, renal tubular degeneration [Hathaway et al. 1991]. At autopsy, rats fed 0.17 g/kg for 90 days showed cloudy swelling and degeneration of kidney tubules and fatty degeneration of the liver [Hathaway et al. 1991].

2. *Effects on Humans:* Diethanolamine causes irritation of the eyes, nose, and throat in humans, and contact of the skin with this substance can cause minor burns of the skin. Splashed into the eye, diethanolamine may cause severe burns [NJDH 1989].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethanolamine may include redness, inflammation, and tearing of the eyes; inflamed eyelids; coughing; and sneezing. Splashed into the eye, this substance may cause severe eye burns, with corneal necrosis and permanent damage.

2. *Chronic exposure:* The signs and symptoms of repeated or prolonged skin contact with diethanolamine include dryness and cracking of the skin and minor burns.

- **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 diethanolamine! ***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.***

   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 diethanolamine 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 diethanolamine and lead to worker exposures to this substance:

—Use as a liquid detergent in cleaners, polishes, textile specialties, paints, cutting oils, and shampoos

—Use as an absorbent for acid gases

—Use as an emulsifier and dispersing agent in various agricultural chemicals, cosmetics, and pharmaceuticals

—Manufacture of rubber chemicals, surface-active ingredients, and petroleum demulsifiers

—Use as a chemical intermediate in the manufacture of resins and plasticizers

—Use as a humectant and softening agent, in the production of lubricants for the textile industry, and in organic syntheses

The following methods are effective in controlling worker exposures to diethanolamine, 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 diethanolamine, the licensed health care professioanl 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 diethanolamine 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 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 recom-

mended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to diethanolamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethanolamine 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 diethanolamine.

- **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 diethanolamine is made using a coated XAD-2 tube (80/40 mg sections, 20/60 mesh); the coating is 10 percent 1-naphthylisothiocyanate (NITC). 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 dimethylformamide to extract the diethanolamine derivative. 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 diethanolamine contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with diethanolamine 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 diethanolamine, particularly its potential to cause skin irritation.

A worker who handles diethanolamine 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 diethanolamine or a solution containing diethanolamine is handled, processed, or stored.

STORAGE

Diethanolamine 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 diethanolamine should be protected from physical damage and should be stored separately from oxidizers, acidic materials, heat, sparks, and open flame. Because containers that formerly contained diethanolamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethanolamine, 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. Mix with inert absorbent materials such as dry sand or vermiculite and place in appropriate containers for disposal.
6. Flush these residues with large quantities of water after neutralizing with sodium bisulfate.

7. Do not flush to sewers or open waterways.

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**

  Diethanolamine 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 diethanolamine; 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 more or otherwise use 10,000 lb or more of diethanolamine per calendar year are required by EPA [40 CFR Part 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of diethanolamine 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 diethanolamine 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 diethanolamine 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 diethanolamine. 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 diethanolamine and may provide protection for periods greater than 8 hours: butyl rubber, neoprene, nitrile rubber, polyvinyl chloride, and Viton®.

If diethanolamine 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 diethanolamine 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 diethanolamine. Contact lenses should not be worn if the potential exists for diethanolamine exposure.

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Occupational Health Guideline for Diethylamine

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: $(C_2H_5)_2NH$
- Synonyms: None
- Appearance and odor: Colorless liquid with a fishy odor, like ammonia.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diethylamine is 25 parts of diethylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 75 milligrams of diethylamine per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for diethylamine a Threshold Limit Value of 3 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diethylamine 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.

- **Effects of overexposure**

1. Short-term Exposure: Diethylamine vapors may cause irritation of the respiratory tract, causing coughing, chest pain, or immediate or delayed breathing difficulties. High vapor concentrations may also cause severe irritation of the eyes. Contact of the liquid with bare skin may cause irritation. Covered contact as with clothing wet with diethylamine may cause skin burns. Contact of the liquid with the eyes is an emergency and may result in serious eye injury.

2. Long-term Exposure: Prolonged or repeated skin contact with liquid diethylamine may cause chronic irritation. Prolonged or repeated contact of the eyes with vapors of diethylamine at levels near the irritant level often results in swelling of the eye, causing foggy vision and the appearance of halos around lights.

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 diethylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diethylamine 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 diethylamine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of diethylamine might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Diethylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Diethylamine is a severe eye irritant and may cause tissue damage. Persons with pre-existing eye problems 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**

Diethylamine vapor is a severe irritant to mucous membranes, eyes, and skin. Rabbits repeatedly exposed to 50 ppm for 7 hours daily showed corneal damage and pulmonary irritation. In one reported human case, liquid splashed into the eye caused immediate intense pain. In spite of emergency irrigation and treatment the cornea became swollen and cloudy. Some permanent

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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visual impairment resulted. Contact with the liquid causes vesiculation and necrosis of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

1. Molecular weight: 73.14
2. Boiling point (760 mm Hg): 55.5 C (132 F)
3. Specific gravity (water = 1): 0.71
4. Vapor density (air = 1 at boiling point of diethylamine): 2.5
5. Melting point: −50 C (−58 F)
6. Vapor pressure at 20 C (68 F): 195 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): 16.9

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids will cause spattering.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving diethylamine.
4. Special precautions: Liquid diethylamine will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Less than −18 C (less than 0 F) (closed cup)
2. Autoignition temperature: 312 C (594 F)
3. Flammable limits in air, % by volume: Lower: 1.8; Upper: 10.1
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: The MCA's *Material Safety Data Sheet* states that "diethylamine has a strong ammoniacal odor which gives good warning of its presence." The Department of Transportation's CHRIS manual for the Coast Guard gives an odor threshold of 0.14 ppm.
2. Eye Irritation Level: Grant reports that "chronic exposure to the vapors at concentrations as low as 50 ppm in air causes conjunctival and pulmonary irritation in rabbits; corneal erosion develops after 2 weeks of exposure." Patty notes that both edema of the cornea and eye irritation have been observed during industrial exposures to diethylamine. The concentrations producing these effects are not given. Permanent eye injury is reported to occur after repeated exposure to 50 ppm, according to Brieger and Hodes.
3. Other Information: The MCA's *Material Safety Data Sheet* states that diethylamine is a respiratory tract irritant, and the AIHA *Hygienic Guide* reports that this compound irritates mucous membranes. No quantitative information is given.
4. Evaluation of Warning Properties: Since the odor threshold of diethylamine (0.14 ppm) is well below the permissible exposure limit, this substance is considered to have 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 in a silica gel tube, followed by desorption with sulfuric acid in methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure diethylamine may be used. An analytical method for diethylamine 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 liquid diethylamine, where skin contact may occur.

• Clothing wet with liquid diethylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diethylamine from the clothing. If the clothing is to be

laundered or otherwise cleaned to remove the diethylamine, the person performing the operation should be informed of diethylamine's hazardous properties.

• Where exposure of an employee's body to liquid diethylamine 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 or non-impervious clothing which becomes contaminated with liquid diethylamine should be removed immediately and not reworn until the diethylamine 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 diethylamine or solutions containing more than 0.5 percent by weight of diethylamine contacting the eyes.

• Employees should be provided with and required to use splash-proof safety goggles where solutions containing 0.5 percent or less of diethylamine by weight may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid diethylamine or solutions containing more than 0.5 percent by weight of diethylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid diethylamine should be immediately washed or showered to remove any diethylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diethylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of textile finishing agents, surfactants, rubber processing chemicals, agricultural chemicals, and pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a corrosion inhibitor in iron, steel, and metal industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as polymerization inhibitor and catalyst in polymer industry; intermediate in dye industry	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as depilatory of animal skins; and in electroplating solutions	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 diethylamine 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 diethylamine gets on the skin, immediately flush the contaminated skin with water. If diethylamine soaks 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 diethylamine, 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 diethylamine 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 diethylamine 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. Diethylamine 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 diethylamine vapors are permitted.

- Waste disposal method:

Diethylamine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR DIETHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
1250 ppm or less	A chemical cartridge respirator with a full facepiece and an cartridge(s) which provide protection against diethylamine. A gas mask with a chin-style or a front- or back-mounted canister which provides protection against diethylamine. 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 diethylamine. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Diethylamino Ethanol

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: $(C_2H_5)_2NC_2H_4OH$
- Synonyms: 2-Diethylaminoethyl alcohol; N,N-diethylethanolamine; diethyl (2-hydroxytriethyl) amine; 2-diethylamino ethanol; 2-hydroxy-triethylamine
- Appearance and odor: Colorless liquid with a weak ammonia odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diethylamino ethanol is 10 parts of diethylamino ethanol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 50 milligrams of diethylamino ethanol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diethylamino ethanol 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: Liquid diethylamino ethanol splashes will cause skin irritation. Liquid splashes in the eye will cause irritation and damage. Diethylamino ethanol vapor may cause nausea and vomiting. It may also cause cough and shortness of breath. Splashes may cause eye and skin irritation.

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 diethylamino ethanol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diethylamino ethanol 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 diethylamino ethanol exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of diethylamino ethanol might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Diethylamino ethanol is a primary skin irritant and a probable skin sensitizer. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Diethylamino ethanol is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems 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**

Diethylamino ethanol vapor is a skin, eye, and respiratory irritant. Rats exposed to 500 ppm 6 hours daily for 5 days exhibited marked eye and nasal irritation, and a number of animals had corneal opacity by the end of the third day; the mortality rate was 20%, and at autopsy there was acute purulent bronchiolitis and bronchopneumonia. Daily exposure at 200 ppm for up to 6 months was fatal in some rats, with death occurring during the first 30 days. An attempt by a laboratory worker to remove animals from an inhalation chamber containing approximately 100 ppm resulted in nausea and vomiting within 5 minutes after a brief exposure; no irritation of the eyes or throat was noted during this

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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brief exposure. Other persons in the same room also complained of a nauseating odor but showed no ill effects. The liquid is a severe skin irritant; in the guinea pig it is a skin sensitizer. It is also a severe eye irritant and may produce permanent eye injury. No systemic effects from human exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 117.2
  2. Boiling point (760 mm Hg): 162 C (324 F)
  3. Specific gravity (water = 1): 0.89
  4. Vapor density (air = 1 at boiling point of diethylamino ethanol): 4.0
  5. Melting point: Data not available
  6. Vapor pressure at 20 C (68 F): 1 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): 0.17
- **Reactivity**
  1. Conditions contributing to instability: Heat.
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids will cause spattering.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving diethylamino ethanol.
  4. Special precautions: Liquid diethylamino ethanol will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 52 C (126 F) (closed cup)
  2. Autoignition temperature: 320 C (608 F)
  3. Flammable limits in air, % by volume: Lower: 6.7; Upper: 11.7
  4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical
- **Warning properties**
  1. Odor Threshold: Diethylamino ethanol has a weak ammoniacal odor, but no information is available concerning its odor threshold.
  2. Eye Irritation Level: The Pennwalt Corporation *Material Safety Data Sheet* states that diethylamino ethanol is irritating to the eyes. Deichmann and Gerarde (in *Toxicology of Drugs and Chemicals*, p. 216) state that 2-diethylamino ethanol as the "undiluted" compound is a severe eye irritant capable of producing permanent eye injury. No information is available, however, concerning air concentrations producing eye irritation.
  3. Other Information: Deichmann and Gerarde report that the vapors of diethylamino ethanol irritate the respiratory tract, but the concentrations producing this irritation are not given.
  4. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties of diethylamino ethanol to air concentrations, 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**

An analytical method for diethylamino ethanol 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 diethylamino ethanol, where skin contact may occur.
- Clothing contaminated with liquid diethylamino ethanol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diethylamino ethanol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diethylamino ethanol, the person performing the operation should be informed of diethylamino ethanol's hazardous properties.
- Where exposure of an employee's body to liquid diethylamino ethanol 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 liquid diethylamino ethanol should be removed immediately and not reworn until the diethylamino ethanol is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of solutions containing 5 percent or more of diethylamino ethanol by weight contacting the eyes and where solutions containing less than 5 percent diethylamino ethanol by weight may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to solutions containing 5 percent or more of diethylamino ethanol by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid diethylamino ethanol should be immediately washed or showered to remove any diethylamino ethanol.

• Employees who handle liquid diethylamino ethanol 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 diethylamino ethanol may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of medicinals and pharmaceuticals, pesticides, protective surface coatings for metals, emulsifying agents for polishes, resinous materials for treating fiber surfaces, fluorescent brightening agents, and in polymer production	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis to prepare compounds for surfactants, detergents, wetting agents, and yarn-treating	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in synthetic fiber dyeing and vat dyes; use as photographic stabilizing solutions	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 diethylamino ethanol 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 diethylamino ethanol gets on the skin, immediately flush the contaminated skin with water. If diethylamino ethanol soaks 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 diethylamino ethanol, 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 diethylamino ethanol 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 diethylamino ethanol 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. Diethylamino ethanol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explo-

sion. Sewers designed to preclude the formation of explosive concentrations of diethylamino ethanol vapors are permitted.

• Waste disposal methods:

Diethylamino ethanol 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.

REFERENCES

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RESPIRATORY PROTECTION FOR DIETHYLAMINO ETHANOL

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
500 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 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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of diethylamino ethanol; 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 DIETHYLENETRIAMINE

INTRODUCTION

This guideline summarizes pertinent information about diethylenetriamine 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**

  $C_4H_{13}N_3$

- **Structure**

  $(NH_2CH_2CH_2)_2NH$

- **Synonyms**

  DETA; N-(2-aminoethyl)1,2-ethanediamine; 2,2'-diaminodiethylamine; aminoethylethandiamine; bis(2-aminoethyl)amine; bis(beta-aminoethyl)amine; N,N-bis(2-aminoethyl)amine; 2,2'-iminobisethylamine

- **Identifiers**

  1. CAS No.: 111-40-0
  2. RTECS No.: IE1225000
  3. DOT UN: 2079 29
  4. DOT label: Corrosive

- **Appearance and odor**

  Diethylenetriamine is a combustible, somewhat viscous, colorless to yellow liquid with an ammonia-like odor. This substance is hygroscopic and strongly alkaline.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 103.17
  2. Boiling point (760 mm Hg): 207°C (405°F)
  3. Specific gravity (water = 1): 0.96 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of diethylenetriamine): 3.56
  5. Melting point: -39°C (-38°F)
  6. Vapor pressure at 20°C (68°F): 0.37 mm Hg
  7. Solubility: Completely soluble in water; soluble in hydrocarbons; insoluble in ether.
  8. Evaporation rate (ether = 1): Greater than 400

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Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of diethylenetriamine with oxidizing materials or strong acids may cause a violent reaction; in contact with cellulose nitrate, this substance ignites spontaneously. In contact with silver, cobalt, or chromium compounds, certain diethylenetriamine complexes can be explosive.

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen and carbon, and hydrocarbons) may be released in a fire involving diethylenetriamine.

4. Special precautions: Diethylenetriamine is corrosive to copper and its alloys.

Flammability

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethylenetriamine.

1. Flash point: 98°C (208°F) (open cup)

2. Autoignition temperature: 358°C (676°F)

3. Flammable limits in air (percent by volume): Lower, 2; upper, 6.7

4. Extinguishant: Use water spray, alcohol foam, carbon dioxide, or dry chemical to fight fires involving diethylenetriamine. 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 diethylenetriamine 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 diethylenetriamine 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 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 a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving diethylenetriamine. Structural firefighters' protective clothing may provide limited protection against fires involving diethylenetriamine.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) had not promulgated a permissible exposure limit (PEL) for diethylenetriamine [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 diethylenetriamine of 1 ppm (4 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek with 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 diethylenetriamine a threshold limit value (TLV) of 1 ppm (4.2 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned diethylenetriamine a "Skin" notation [ACGIH 1993].

- **Rationale for limits**

The NIOSH and ACGIH limits are based on the risk of skin and respiratory tract irritation and sensitization associated with exposure to diethylenetriamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to diethylenetriamine can occur through inhalation, ingestion, eye or skin contact, and percutaneous absorption.

- **Summary of toxicology**

1. *Effects on Animals:* Diethylenetriamine is a severe irritant of the eyes and skin in animals. Application of this substance to rabbit skin caused severe injury, and instillation into the eyes of rabbits caused maximum damage to the cornea [Clayton and Clayton 1981; Grant 1986]. The dermal LD_{50} in rabbits is 1,090 mg/kg [NIOSH 1994]. Acutely poisoned animals convulsed and exhibited signs of gastrointestinal irritation before death [NIOSH 1994]. Rats exposed once to a 300-ppm concentration of diethylenetriamine for 8 hours survived [ACGIH 1986]. The oral LD_{50} in rats is 1,080 mg/kg [NIOSH 1994].

2. *Effects on Humans:* Diethylenetriamine is a severe irritant of the eyes, skin, mucous membranes, and upper respiratory tract and a potent skin and pulmonary sensitizer in humans. In contact with the skin, diethylenetriamine causes severe irritation, with edema and sometimes necrosis [Grant 1986]. A majority of workers chronically exposed to this substance are reported to develop sensitization to it. Exposure to the heated vapor of diethylenetriamine (concentration not specified) causes respiratory tract irritation, and pulmonary sensitization is reported to occur with "relatively high frequency" [NLM 1993; ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethylenetriamine vapors include eye and respiratory tract irritation, with tearing and redness of the eyes, coughing, and difficult breathing. Contact of the eyes or skin with the liquid causes corneal or skin burns, with blistering, swelling, redness, and cell death.

2. *Chronic exposure*: Repeated exposure to diethylenetriamine may cause an asthmatic response in sensitized individuals. Repeated contact of the skin with this substance may cause dermatitis, with redness and scaling, or skin sensitization, accompanied by redness, itching, and the development of wheals.

- **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 diethylenetriamine! ***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 diethylenetriamine 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 diethylenetriamine and lead to worker exposures to this substance:

—Use as a solvent for sulfur, acid gases, and various resins and dyes

—Use as a saponification agent for acidic materials and as a fuel component

—Use as an intermediate in the manufacture of pharmaceuticals

The following methods are effective in controlling worker exposures to diethylenetriamine, 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 diethylenetriamine, 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 diethylenetriamine 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 pulmonary or 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 diethylenetriamine exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethylenetriamine 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 diethylenetriamine.

- **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 diethylenetriamine is made using a coated XAD-2 tube (80/40 mg sections, 20/60 mesh); the coating is 10 percent (w/w) 1-naphthylisothiocyanate (NITC). 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 dimethylformamide to extract the diethylenetriamine. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method has a sampling and analytical error of 0.10 and is included in the *OSHA Analytical Methods Manual* as OSHA Method No. 60 [OSHA 1985].

PERSONAL HYGIENE

If diethylenetriamine contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then by wash with soap and water.

Clothing contaminated with diethylenetriamine 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 diethylenetriamine, particularly its potential to cause burns of the eyes and skin.

A worker who handles diethylenetriamine 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 diethylenetriamine or a solution containing diethylenetriamine is handled, processed, or stored.

STORAGE

Diethylenetriamine should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication stan-

dard [29 CFR 1910.1200]. Storage should be in low-fire-risk areas, out of direct sunlight. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of diethylenetriamine should be protected from physical damage and should be stored separately from acids, strong oxidizing agents, heat, sparks, and open flame. Because containers that formerly contained diethylenetriamine may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethylenetriamine, 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. Use water spray to reduce vapors; do not get water inside the container.
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 diethylenetriamine for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous quantities, 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**

Diethylenetriamine 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 diethylenetriamine; 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 diethylenetriamine 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 diethylenetriamine 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 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 diethylenetriamine 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 any skin contact with diethylenetriamine. 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 diethylenetriamine and may provide protection for periods greater than 8 hours: butyl rubber, neoprene, and Viton . Natural rubber, nitrile rubber, polyvinyl alcohol, and polyvinyl chloride are not recommended.

If diethylenetriamine 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 diethylenetriamine 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 diethylenetriamine. Contact lenses should not be worn if the potential exists for diethylenetriamine exposure.

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ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

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OSHA [1985]. OSHA analytical methods manual. Salt Lake City, UT: U.S. Department of Labor, OSHA Analytical Laboratory, P. O. Box 65200, 1781 South 300 West, Salt Lake City, Utah 84165-0200.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIETHYL PHTHALATE

INTRODUCTION

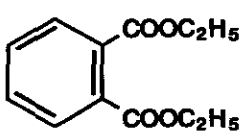
This guideline summarizes pertinent information about diethyl phthalate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations 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**

$C_6H_4(COOC_2H_5)_2$

- **Structure**



- **Synonyms**

1,2-Benzenedicarboxylic acid diethyl ester; Anozol; DEP; diethyl o-phthalate; Estol 1550; ethyl phthalate; Neantine; Palatinol A; phthalic acid, diethyl ester; Phthalol; Placidol E; Solvanol; Unimoll DA.

- **Identifiers**

1. CAS No.: 84-66-2
2. RTECS No.: TI1050000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Diethyl phthalate is a flammable, clear, colorless, oily liquid with a bitter, disagreeable taste and a slight ester odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 222.24
2. Boiling point (760 mm Hg): 298°C (568.4°F)
3. Specific gravity (water = 1): 1.12 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of diethyl phthalate): 7.66
5. Melting point: -40.5°C (-40°F)
6. Vapor pressure at 163°C (325°F): 14 mm Hg
7. Solubility: Insoluble in water; miscible with alcohols,

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ketones, esters, and aromatic hydrocarbons; partly miscible with aliphatic solvents.

8. Evaporation rate (ether = 1): Greater than 300

- **Reactivity**

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of diethyl phthalate with strong acids, strong oxidizing agents, nitric acid, permanganates, or water causes a violent reaction.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, carbon dioxide, and various hydrocarbons) may be released in a fire involving diethyl phthalate.

4. Special precautions: Diethyl phthalate attacks some forms of plastic.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to diethyl phthalate.

1. Flash point: 163°C (325°F) (open cup)

2. Autoignition temperature: 457°C (855°F)

3. Flammable limits in air (percent by volume): Lower, 0.7 (@368°F); upper, data not available

4. Extinguishant: Use dry chemical, water spray, alcohol foam, or carbon dioxide to fight fires involving diethyl phthalate. Water spray and foam are effective but may cause frothing. Water may be used to cool fire-exposed containers.

Fires involving diethyl phthalate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Cool 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 diethyl phthalate.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diethyl phthalate [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 [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diethyl phthalate 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 mild toxic effects and smaller than normal fetuses in animals associated with diethyl phthalate exposure; the ACGIH limit is based on the risks of polyneuritis and vestibular dysfunction associated with exposure to diethyl phthalate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to diethyl phthalate causes irritation of the eyes, mucous membranes, and skin and may have reproductive effects in animals. Applied to the skin of rats, 50% of a 30- to 40-mg/kg dose of diethyl phthalate was excreted unchanged within 1 week, and the unexcreted dose remained in the area of application [Hathaway et al. 1991]. Instilled into rabbit eyes, diethyl phthalate caused mild irritation. Guinea pigs exposed to a 511-ppm concentration of diethyl phthalate for 6 hr showed signs of mild skin irritation, and cats exposed to a 10-mg/L concentration of this substance for 5 hr showed signs of nasal irritation [Clayton and Clayton 1981]. The oral LD_{50} is 8,600 mg/kg in rats and 6,172 mg/kg in mice [NIOSH 1993]. Male rats and mice given diethyl phthalate by oral administration developed testicular and other reproductive effects [NIOSH 1993; HSDB 1992]. Diethyl phthalate is mutagenic in bacterial test systems [NIOSH 1993].

2. *Effects on Humans:* Diethyl phthalate has irritant effects on the eyes, mucous membranes, and skin of humans and also causes central nervous system effects in exposed workers. Exposure to the heated vapors of diethyl phthalate is reported to have caused transient nose and throat irritation [ACGIH 1991]. In a study of Russian workers exposed to several phthalates (butyl phthalate, higher alkyl phthalates, dioctyl phthalate, diisooctyl phthalate, and benzyl butyl phthalate) at average ambient concentrations of 1.7 to 66 mg/m^3, 32% of workers were found to have signs and symptoms of polyneuritis; 78% of those workers who reported experiencing adverse effects also showed signs of vestibular dysfunction. The toxic effects seen in these workers were related to the duration of exposure and occurred only after 6 or 7 years of exposure to this group of phthalates [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to diethyl phthalate include redness and inflammation of eyes and eyelids, runny nose, scratchy throat, headache, dizziness, and nausea.

2. *Chronic exposure:* Chronic exposure to diethyl phthalate may cause signs and symptoms associated with polyneuritis and vestibular dysfunction, including pain, numbness, weakness, and spasms in the arms and legs, dizziness, and nausea.

- **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 from concentrated solutions, vapors, mists, or aerosols of diethyl phthalate. ***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:* Seek medical attention and take the following steps if a large amount of diethyl phthalate 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.

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 diethyl phthalate and lead to worker exposures to this substance:

—Use as a solvent for cellulose acetate in the manufacture of varnishes and dopes

—Use as an alcohol denaturant

—Use as a mosquito repellant, plasticizer in solid rocket propellants, wetting agent, and camphor substitute

—Use as a fixative and solvent in perfumes

The following methods are effective in controlling worker exposures to diethyl phthalate, 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 period 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 diethyl phthalate, 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 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 diethyl phthalate 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 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 diethyl phthalate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diethyl phthalate 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 diethyl phthalate.

- **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 diethyl phthalate is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) and a 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. The sample is then treated with carbon disulfide to extract the diethyl phthalate. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Chemical Information System [OSHA 1990].

PERSONAL HYGIENE

If diethyl phthalate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, followed by washing with soap and water.

Clothing contaminated with diethyl phthalate 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 diethyl phthalate, particularly its potential to be irritating to the skin and eyes.

A worker who handles diethyl phthalate 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 diethyl phthalate or a solution containing diethyl phthalate is handled, processed, or stored.

STORAGE

Diethyl phthalate 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 diethyl phthalate should be protected from physical damage and should be stored separately from acids, bases, strong oxidizing agents, moisture, heat, sparks, and open flame. Because containers that formerly contained diethyl phthalate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diethyl phthalate, 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. Ventilate the area of the spill or leak.
3. Take up small spills with paper or other absorbent material for disposal.
4. Build a dike far ahead of the spill area to contain the spill 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**

  Diethyl phthalate 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 diethyl phthalate is 1,000 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 who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of diethyl phthalate 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 diethyl phthalate 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. Diethyl phthalate 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. U088. It is approved for land disposal as long as the concentration of diethyl phthalate in the waste or treatment residual does not exceed 28-mg/kg. Diethyl phthalate 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 diethyl phthalate 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

prolonged or repeated skin contact with diethyl phthalate. 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. 4H (PE/EVAL) has been recommended for use against permeation by diethyl phthalate and may provide protection for more than 4 but fewer than 8 hr. 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 diethyl phthalate.

If diethyl phthalate 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 diethyl phthalate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and washing facilities should be available within the immediate work area whenever the potential exists for eye or skin contact with diethyl phthalate. Contact lenses should not be worn if the potential exists for diethyl phthalate exposure.

REFERENCES CITED

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NIOSH [1993]. Registry of toxic effects of chemical substances: diethyl phthalate. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

NLM [1992]. The hazardous substances data bank: diethyl phthalate. Bethesda, MD: National Library of Medicine.

OSHA [1990]. Computerized information system. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.

Sittig M [1991]. Handbook of toxic and hazardous chemicals. 3rd ed. Park Ridge, NJ: Noyes Publications.

Occupational Health Guideline for Difluorodibromomethane (Freon 12B2)

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: CBr_2F_2
- Synonyms: Dibromodifluoromethane; Freon 12B2
- Appearance and odor: Colorless liquid or gas with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Freon 12B2 is 100 parts of Freon 12B2 per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 860 milligrams of Freon 12B2 per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Freon 12B2 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 Freon 12B2 may cause irritation of the nose and throat, drowsiness, unconsciousness, and death. Exposure may also cause liver damage. If the liquid gets on the skin or in the eyes, it may cause frostbite.

- **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 Freon 12B2.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Freon 12B2 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 Freon 12B2 exposure.

—Liver disease: Although Freon 12B2 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.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Freon 12B2 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**

Freon 12B2 vapor is a respiratory irritant and a narcotic. Rats exposed to 4000 ppm for 15 minutes showed pulmonary edema, while 2300 ppm daily for 6 weeks resulted in the death of more than half the animals. At 2300 ppm dogs showed rapid and progressive signs of intoxication, with weakness and loss of balance after a few days' exposure, followed by convulsions. These dogs at autopsy had pulmonary congestion, centrolobular necrosis of the liver, and some evidence of central nervous system damage. However, other dogs tolerated daily exposures of 350 ppm for 7 months without signs of intoxication. No systemic effects have been reported from industrial exposures. In liquid form, this substance may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 209.8

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

2. Boiling point (760 mm Hg): 24.5 C (76.1 F)
3. Specific gravity (water = 1): 2.46
4. Vapor density (air = 1 at boiling point of Freon 12B2): 7.2
5. Melting point: −141.6 C (−223 F)
6. Vapor pressure at 20 C (68 F): 620 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Higher than 1

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Freon 12B2 reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide and hydrogen fluoride) may be released when Freon 12B2 decomposes.
4. Special precautions: Liquid Freon 12B2 will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Freon 12B2 does not have adequate warning properties. Freon 12B2 is not a known 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 Freon 12B2 vapors using an adsorption tube with subsequent desorption with isopropyl alcohol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure Freon 12B2 may be used. An analytical method for Freon 12B2 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 Freon 12B2.

• Non-impervious clothing which becomes wet with liquid Freon 12B2 should be removed promptly and not reworn until the Freon 12B2 has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid Freon 12B2 may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to Freon 12B2 may occur and control methods which may be effective in each case:

Operation	Controls
Use as a fire extinguishing agent; use in organic synthesis	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in processing cutting tools as razor blades, hypodermic needles, scalpels, culinary knives, and garden tools	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a special solvent for preparation of explosive mixtures	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 Freon 12B2 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 Freon 12B2 gets on the skin, immediately flush the contaminated skin with water if the liquid Freon 12B2 has not already evaporated. If liquid Freon 12B2 soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of Freon 12B2, 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 Freon 12B2 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 until cleanup has been completed.

• If Freon 12B2 is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If the gas is leaking, stop the flow.
3. If the liquid is spilled or leaked, allow to vaporize.

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RESPIRATORY PROTECTION FOR FREON 12B2

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2500 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 2500 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.

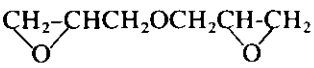
*Only NIOSH-approved or MSHA-approved equipment should be used.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIGLYCIDYL ETHER POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about diglycidyl ether (DGE) 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:** $C_6H_{10}O_3$
- **Structure:** 

- **Synonyms:** Bis(2,3-epoxypropyl) ether; DGE; di(2,3--epoxypropyl) ether; di(2,3-epoxy)propyl ether
- **Identifiers:** CAS 2238-07-05; RTECS KN2350000; DOT not assigned
- **Appearance and odor:** Colorless liquid with a strong, irritating odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 130.16
2. Boiling point (at 760 mmHg): 260°C (500°F)
3. Specific gravity (water = 1): 1.26
4. Vapor density (air = 1 at boiling point of DGE): 4.49
5. Vapor pressure at 25°C (77°F): 0.09 mmHg
6. Saturation concentration in air (approximate) at 25°C (77°F): 0.0121% (121 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Ethers as a class tend to form peroxides upon contact with air and exposure to light.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving DGE.
3. Caution: DGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 64°C (147°F)
2. Extinguishant: Dry chemical, carbon dioxide, alcohol foam
3. Class IIIA Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

1. Odor threshold: Approximately 5 ppm
2. Eye irritation levels: 10 ppm
3. 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 DGE is 0.5 parts of DGE per million parts of air (ppm) [2.8 milligrams of DGE per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded. The National Institute for Occupational Safety and Health (NIOSH) recommends that DGE 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 0.2 ppm (1 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 0.1 ppm (0.5 mg/m³) as a time-weighted average (TWA) concentration 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 diglycidyl ether

	Exposure limits	
	ppm	mg/m³
OSHA PEL Ceiling	0.5	2.8
NIOSH REL (Ca)*		
Ceiling (15 min)	0.2	1
ACGIH TLV® TWA	0.1	0.5

* (Ca): NIOSH recommends treating as a potential human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

DGE 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 DGE caused central nervous system depression, incoordination, breathing difficulty (dyspnea), respiratory failure, and death. In rats and rabbits, acute or subchronic inhalation or dermal administration of DGE produced weight loss, corneal opacities, testicular degeneration, and abnormalities of the blood-forming tissues including lymphoid atrophy of the thymus and depression of white blood cell and bone marrow cell counts. In skin-painting studies, DGE produced tumors in mice. DGE was mutagenic in bacterial test systems.

• Signs and Symptoms of exposure

1. *Short-term (acute):* Exposure to DGE can cause skin burns and severe irritation of the skin, eyes, and respiratory tract.
2. *Long-term (chronic):* Exposure to DGE can cause dermatitis and skin sensitization.

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 DGE, 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, reproductive, respiratory, nervous, 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 DGE 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 DGE. 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, 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. Because occupational exposure to DGE may cause adverse reproductive effects or 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 DGE. 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 DGE vapors with charcoal adsorption tubes followed by desorption with methylene chloride and analysis by gas chromatography. Refer to the *Criteria for Recommended Standard. . . . Occupational Exposure to Glycidyl Ethers* for limitations and correct use of this method. Direct-reading devices calibrated to measure DGE may also be used if available.

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 DGE.

SANITATION

Clothing which is contaminated with DGE 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 DGE from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DGE'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 DGE 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 DGE should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

DGE is not generally used outside of research laboratories. There are no common industrial uses for DGE.

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 DGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DGE 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 DGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DGE gets on the skin, wash it immediately with soap and water. If DGE 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 DGE 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 DGE, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing DGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing DGE 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 diglycidyl 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 or self-contained breathing apparatus

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

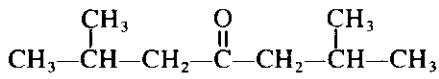
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIISOBUTYL KETONE

INTRODUCTION

This guideline summarizes pertinent information about diisobutyl ketone 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:** $C_9H_{18}O$
- **Structure:**



- **Synonyms:** DBK; diisopropyl acetone; 2,6-dimethyl-4-heptanone; isovalerone; valerone
- **Identifiers:** CAS 108-83-8; RTECS MJ5775000; DOT 1157, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a mild ketone odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 142.27
2. Boiling point (at 760 mmHg): 169.4°C (336.9°F)
3. Specific gravity (water = 1): 0.81
4. Vapor density (air = 1 at boiling point of diisobutyl ketone): 4.9
5. Melting point: -46°C (-51°F)
6. Vapor pressure: At 20°C (68°F), 1.7 mm Hg; at 25°C (77°F), 2.4 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.05
8. Evaporation rate (butyl acetate = 1): 0.17
9. Saturation concentration in air (approximate): At 20°C (68°F), 0.22% (2,200 ppm); at 25°C (77°F), 0.32% (3,200 ppm)

- **Reactivity**

1. Incompatabilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving diisobutyl ketone.
3. Caution: Diisobutyl ketone will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 60°C (140°F) (closed cup)
2. Autoignition temperature: 396°C (745°F)
3. Flammable limits in air, % by volume at 100°C: Lower, 0.8; upper, 7.1
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.11 ppm
2. Eye irritation level: 25 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, diisobutyl ketone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, diisobutyl ketone is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for diisobutyl ketone is 50 parts of diisobutyl ketone per million parts of air (ppm) [290 milligrams of diisobutyl ketone 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 (140 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 (150 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 diisobutyl ketone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	50	290
NIOSH REL TWA	25	140
ACGIH TLV® TWA	25	150

HEALTH HAZARD INFORMATION

• **Routes of exposure**

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

• **Summary of toxicology**

Effects on animals: Acute inhalation or oral administration of diisobutyl ketone by rats or guinea pigs caused drowsiness, impaired muscular coordination (ataxia), damage to the lungs, liver, or kidneys, and death.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to diisobutyl ketone can cause headache, dizziness, drowsiness, tearing, and irritation of the eyes, nose, and throat.

2. *Long-term (chronic):* Exposure to diisobutyl ketone 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 diisobutyl ketone, 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 diisobutyl ketone 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 diisobutyl ketone. 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 diisobutyl ketone 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 diisobutyl ketone 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 diisobutyl ketone may also be used if available. A detailed sampling and analytical method for diisobutyl ketone 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 diisobutyl ketone.

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

SANITATION

Clothing which is contaminated with diisobutyl ketone 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 diisobutyl ketone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of diisobutyl ketone's hazardous properties.

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

Skin that becomes contaminated with diisobutyl ketone 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 diisobutyl ketone 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 diisobutyl ketone 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 diisobutyl ketone

Operations	Controls
During use as a paint thinner; during use as a solvent in the production of synthetic coatings, soap, or nitrocellulose	General dilution ventilation, local exhaust ventilation, personal protective equipment
During use as an intermediate in organic synthesis, an extractant in the pharmaceutical industry, a separating agent in the chemical industry, or a dispersant in the manufacture of resins	General dilution ventilation, 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 diisobutyl ketone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If diisobutyl ketone 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 diisobutyl ketone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If diisobutyl ketone gets on the skin, wash it immediately with soap and water. If diisobutyl ketone 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 diisobutyl ketone 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 diisobutyl ketone, 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 diisobutyl ketone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing diisobutyl ketone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Diisobutyl ketone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing diisobutyl ketone 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 diisobutyl ketone

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 2,000 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 2,000 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 25 ppm (140 mg/m³) (TWA).

Occupational Health Guideline for Diisopropylamine

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: $(CH_3)_2CH\text{-}NH\text{-}CH(CH_3)_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with an odor like ammonia.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diisopropylamine is 5 parts of diisopropylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 20 milligrams of diisopropylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diisopropylamine 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.

- **Effects of overexposure**

1. Short-term Exposure: Diisopropylamine may cause headache, visual problems and nausea. It may also cause irritation of the respiratory tract.

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 diisopropylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diisopropylamine 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 diisopropylamine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of diisopropylamine might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Diisopropylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Diisopropylamine is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems 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**

Diisopropylamine vapor is a respiratory irritant and a severe eye irritant. Exposure of experimental animals to 260 to 2200 ppm for several hours resulted in fatalities at the higher concentrations as a result of severe pulmonary damage; exposure at these concentrations for several hours caused clouding of the cornea which was reversible. Workers exposed to concentrations between 25 and 50 ppm complained of nausea, headache, and disturbances in vision. Diisopropylamine has been reported to cause skin irritation in animals.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 101.2
  2. Boiling point (760 mm Hg): 84 C (183 F)
  3. Specific gravity (water = 1): 0.72

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. Vapor density (air = 1 at boiling point of diisopropylamine): 3.5

5. Melting point: −96 C (−141 F)

6. Vapor pressure at 20 C (68 F): 60 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions below 27 C (81 F). Above this temperature, the maximum solubility is 30%.

8. Evaporation rate (butyl acetate = 1): 5.8

• **Reactivity**

1. Conditions contributing to instability: Heat.

2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids will cause spattering.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving diisopropylamine.

4. Special precautions: Liquid diisopropylamine will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: −6.7 C (20 F) (closed cup)

2. Autoignition temperature: 316 C (600 F)

3. Flammable limits in air, % by volume: Lower: 0.8; Upper: 7.1

4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: Diisopropylamine has an odor like ammonia, but no quantitative information is available concerning its odor threshold.

2. Eye Irritation Level: Grant reports that visual disturbances have been observed in men who have been exposed to concentrations of 25 to 50 ppm diisopropylamine. "Experimental exposures of rabbits, guinea pigs, rats, and cats have established that the vapor is injurious to the corneal epithelium." According to Grant, "this is presumably the cause of the visual disturbances observed in men." A several-hour exposure to concentrations of 260 to 2200 ppm has caused corneal injury to experimental animals.

3. Other Information: The *Documentation of TLV's* reports that Treon et al. observed irritation of the respiratory mucous membranes in animals exposed repeatedly to 260 ppm.

4. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of diisopropylamine, 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 diisopropylamine 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 repeated or prolonged skin contact with liquid diisopropylamine.

• Clothing wet with liquid diisopropylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diisopropylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diisopropylamine, the person performing the operation should be informed of diisopropylamine's hazardous properties.

• Any clothing which becomes wet with liquid diisopropylamine should be removed immediately and not reworn until the diisopropylamine is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of solutions containing 5 percent or more of diisopropylamine by weight contacting the eyes and where solutions containing less than 5 percent of diisopropylamine by weight may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to solutions containing 5 percent or more of diisopropylamine by weight, an eye-wash foun-

tain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes wet with liquid diisopropylamine should be promptly washed or showered to remove any diisopropylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to diisopropylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of corrosion inhibitors in iron and steel	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in synthesis of herbicides, delayed action vulcanization accelerator for sulfur-cured rubbers; as a catalyst for chemical synthesis of alkylene cyanohydrin	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as component in gels for cosmetic and medical applications as deodorants and aftershave solutions	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 diisopropylamine 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 diisopropylamine gets on the skin, immediately wash the contaminated skin with water. If diisopropylamine soaks through the clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of diisopropylamine, 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 diisopropylamine 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 diisopropylamine 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. Diisopropylamine 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 diisopropylamine vapors are permitted.

• Waste disposal method:

Diisopropylamine 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 DIISOPROPYLAMINE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 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 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 Health Guideline for Dimethyl Acetamide

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: $CH_3CON(CH_3)_2$
- Synonyms: N,N-dimethyl acetamide; DMAC
- Appearance and odor: Colorless liquid with a faint, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethyl acetamide is 10 parts of dimethyl acetamide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of dimethyl acetamide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethyl acetamide 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**

Repeated or prolonged exposure to dimethyl acetamide may cause liver damage with yellow jaundice. Repeated exposure at high concentrations may cause depression, drowsiness, confusion, and hallucinations.

- **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 dimethyl acetamide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethyl acetamide 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.

—Liver function tests: Since liver damage has been observed in humans exposed to dimethyl acetamide, a profile of liver function should be obtained by using 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**

Inhalation of the vapor or skin absorption of the liquid causes liver damage. Repeated dermal application of the liquid to dogs at a dosage level of 4.0 ml/kg for 6 weeks caused severe fatty infiltration of the liver. Repeated exposure of rats to a concentration of 195 ppm for 6 months resulted in focal necrosis of the liver; exposure to 40 ppm for the same period of time caused no adverse effects. Workers repeatedly exposed to 20 to 25 ppm developed jaundice; appreciable skin absorption was thought to have occurred. Dimethyl acetamide has a significant antitumor effect in animals. Nine patients with neoplastic disease were given daily doses of 400 mg/kg by an unspecified route for 3 or more days as a therapeutic trial; they experienced depression, lethargy, confusion, and disorientation; on the last (4th or 5th) day of therapy or within 24 hours thereafter, the patients had visual and auditory hallucinations, perceptual distortions, and at times delusions; after 24 hours these gradually subsided.

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: 87.1
2. Boiling point (760 mm Hg): 166 C (331 F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of dimethyl acetamide): 3.0
5. Melting point: −20 C (−4 F)
6. Vapor pressure at 20 C (68 F): 1.5 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): Less than 0.17

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 350 C (662 F) cause decomposition and development of pressure in closed containers.
2. Incompatibilities: Contact with carbon tetrachloride and other halogenated compounds, particularly when in contact with iron, may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as dimethylamine and carbon monoxide) may be released in a fire involving dimethyl acetamide.
4. Special precautions: Dimethyl acetamide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 70 C (158 F) (open cup)
2. Autoignition temperature: 490 C (914 F)
3. Flammable limits in air, % by volume: Lower: 1.8 (at 212 F); Upper: 11.5 (at 320 F)
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide. Do not use halogenated extinguishing media.

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Eye Irritation Level: Grant states that "on decomposition, it is said to emit fumes which are highly irritating to the eyes and mucous membranes." He reports that it causes mild, reversible injury graded 3 on a scale of 10 when tested on rabbit eyes.
3. Evaluation of Warning Properties: Since no quantitative information is available relating its warning properties to air concentrations, 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 dimethyl acetamide vapors using a silica gel tube, followed by desorption with methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dimethyl acetamide may be used. An analytical method for dimethyl acetamide 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 liquid dimethyl acetamide.
- Clothing contaminated with dimethyl acetamide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dimethyl acetamide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dimethyl acetamide, the person performing the operation should be informed of dimethyl acetamide's hazardous properties.
- Where exposure of an employee's body to dimethyl acetamide 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 dimethyl acetamide should be removed immediately and not reworn until the dimethyl acetamide is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid dimethyl acetamide may contact the eyes.

SANITATION

• Skin that becomes contaminated with dimethyl acetamide should be immediately washed or showered to remove any dimethyl acetamide.

• Eating and smoking should not be permitted in areas where liquid dimethyl acetamide is handled, processed, or stored.

• Employees who handle liquid dimethyl acetamide 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 dimethyl acetamide may occur and control methods which may be effective in each case:

Operation	Controls
Use as a spinning solvent for synthetic fibers; as a solvent for film casting and top coating resins	Local exhaust ventilation; personal protective equipment
Use as a reaction medium and catalyst; as an extraction solvent for recovery and purification of butadiene; use as a crystallization and purification solvent; as a paint stripping solvent; during recovery and purification from top coating, film casting, spinning, and chemical processes	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 dimethyl acetamide 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 dimethyl acetamide gets on the skin, immediately flush the contaminated skin with water. If liquid dimethyl acetamide soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention promptly.

• **Breathing**

If a person breathes in large amounts of dimethyl acetamide, 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 dimethyl acetamide 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.

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 dimethyl acetamide 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:

Dimethyl acetamide may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in sealed containers 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 DIMETHYL ACETAMIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
100 ppm or less	Any supplied-air respirator.**
	Any self-contained breathing apparatus.**
400 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 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.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of dimethyl acetamide; 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 400 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Dimethylamine

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: $(CH_3)_2NH$
- Synonyms: Dimethylamine, anhydrous
- Appearance and odor: Colorless liquid or gas with a pungent, fishy, or ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethylamine is 10 parts of dimethylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 18 milligrams of dimethylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethylamine 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: Dimethylamine vapor may cause irritation of the lungs, nose, throat, and eyes. It may cause coughing and sneezing. Contact with the liquid may cause skin and eye burns.

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 dimethylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethylamine 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 dimethylamine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of dimethylamine might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Dimethylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Dimethylamine is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems 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**

Dimethylamine gas is a severe respiratory, eye, and mucous membrane irritant in animals. Animals repeatedly exposed to concentrations of approximately 100 to 200 ppm for 18-20 weeks showed marked irritation of the respiratory tract with pulmonary edema as well as hepatic injury, including centrolobular necrosis; corneal injury was observed in guinea pigs and rabbits after 9 days of exposure. Various species survived 5 ppm of continuous exposure for 90 days without signs of toxicity, but at autopsy some showed mild inflammatory changes in the lungs. A drop of undiluted dimethylamine placed on a rabbit's cornea caused the cornea to become as white as the sclera in 1 minute. Both the liquid and the vapor are highly irritating to the eyes and may result in loss of visual acuity. Dermatitis and conjunctivitis are occasionally observed in chemical workers after prolonged exposure to the gas. No sys-

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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temic effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 45.1
  2. Boiling point (760 mm Hg): 6.9 C (44.4 F)
  3. Specific gravity (water = 1): 0.68 (liquid at 0 C)
  4. Vapor density (air = 1 at boiling point of dimethylamine): 1.6
  5. Melting point: −92 C (−134 F)
  6. Vapor pressure at 20 C (68 F): 1.72 atm.
  7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
  8. Evaporation rate (butyl acetate = 1): Greater than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers, chlorine, and mercury 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 dimethylamine.
  4. Special precautions: Liquid dimethylamine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Not pertinent (gas)
  2. Autoignition temperature: 402 C (755 F)
  3. Flammable limits in air, % by volume: Lower: 2.8; Upper: 14.4
  4. Extinguishant: Stop flow of gas.
- **Warning properties**
  1. Odor Threshold: Summer reports that the odor threshold of dimethylamine is 6 ppm, and May reports two odor thresholds, .021 and 23 ppm.
  2. Eye Irritation Level: The *Documentation of TLV's* reports that dimethylamine irritates mucous membranes. Repeated exposures of guinea pigs and rabbits to concentrations of 183 to 97 ppm dimethylamine have resulted in corneal injury. There is no available information on the threshold of eye irritation.
  3. Other Information: The *Documentation of TLV's* states that dimethylamine is a mucous membrane irritant and a respiratory tract irritant. The thresholds of irritation are not given.
  4. Evaluation of Warning Properties: Since the odor threshold ranges between one-five hundredth of the permissible exposure limit and approximately twice the permissible exposure limit, dimethylamine 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 in a silica gel tube, followed by desorption with sulfuric acid in methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dimethylamine may be used. An analytical method for dimethylamine 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 dimethylamine.
- 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 dimethylamine.
- Clothing wet with solutions containing dimethylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dimethylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to

remove the dimethylamine, the person performing the operation should be informed of dimethylamine's hazardous properties.

- Where there is any possibility of exposure of an employee's body to liquid dimethylamine, 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 liquid solutions of dimethylamine should be removed promptly and not reworn until the dimethylamine is removed from the clothing.
- Any clothing which becomes wet with liquid dimethylamine or liquid solutions of dimethylamine should be removed immediately and not reworn until the dimethylamine 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 dimethylamine or solutions containing dimethylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid dimethylamine or solutions containing dimethylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid dimethylamine should be immediately washed or showered to remove any dimethylamine.
- Skin that becomes contaminated with solutions containing dimethylamine should be promptly washed or showered to remove any dimethylamine.
- Employees who handle dimethylamine or solutions containing dimethylamine 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 dimethylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of spinning solvents for acrylic and polymeric fibers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as raw material in synthesis of agricultural chemicals; vulcanization accelerators for sulfur-cured rubber; softeners, lubricants; textile water-proofing agents; cationic surfactants; pharmaceuticals; detergents and soaps; as an antioxidant	Process enclosure; general dilution ventilation; personal protective equipment
Use as a general solvent; acid gas absorbent and flotation agent in manufacture of dyes and in electroplating	Process enclosure; general dilution ventilation; personal protective equipment
Use as photographic chemical, plasticizer, and ion exchange agent	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a stabilizer in natural rubber latex	Process enclosure; general dilution ventilation; local exhaust ventilation
Use as a stabilizer for certain types of resins (polymerization inhibitor)	General dilution ventilation; local exhaust ventilation
Use as a retarder in spinning bath of rayon (for tire cord)	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a component of rocket propellants; as an antiknock agent in other fuels	General dilution ventilation; 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 dimethylamine 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 dimethylamine gets on the skin, immediately flush the contaminated skin with water. If dimethylamine soaks through the clothing, remove the clothing immediately

and wash the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of dimethylamine, 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 dimethylamine 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 dimethylamine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or 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:

Dimethylamine 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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RESPIRATORY PROTECTION FOR DIMETHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
500 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) which provides protection against dimethylamine. A gas mask with a chin-style or a front- or back-mounted canister which provides protection against dimethylamine. 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 dimethylamine. Any escape self-contained breathing apparatus.

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

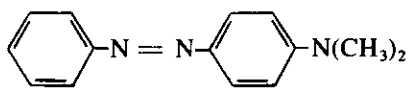
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 4-DIMETHYLAMINOAZOBENZENE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 4-dimethylaminoazobenzene 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:** $C_{14}H_{15}N_3$
- **Structure:**



- **Synonyms:** N,N-Dimethyl-4-aminoazobenzene; N,N-dimethyl-4-(phenylazo)-benzenamine; p-dimethylaminoazobenzene; N,N-dimethyl-p-phenylazoaniline; benzeneazodimethylaniline; methyl yellow; DAB
- **Identifiers:** CAS 60-11-7; RTECS BX7350000; DOT not assigned.
- **Appearance:** Yellow leaf-shaped crystals

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 225.32
2. Boiling point (at 760 mmHg): Sublimes
3. Vapor density (air = 1 at boiling point of 4-dimethylaminoazobenzene): 7.78
4. Melting point: 116°C (240°F)
5. Vapor pressure: Negligible
6. Insoluble in water

- **Reactivity**

Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving 4-dimethylaminoazobenzene.

- **Flammability**

Extinguishant: Alcohol foam, carbon dioxide, or dry chemical

- **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-dimethylaminoazobenzene; however, the OSHA standard requires implementation of stringent controls wherever 4-dimethylaminoazobenzene or solid or liquid mixtures containing at least 0.1% by weight or volume of 4-dimethylaminoazobenzene 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 1910.1015, 4-Dimethylaminoazobenzene. 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 a threshold limit value (TLV®) for 4-dimethylaminoazobenzene.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

4-Dimethylaminoazobenzene may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

Effects on animals: Acute or oral administration of 4-dimethylaminoazobenzene to rats caused liver degeneration. Subchronic and chronic intraperitoneal injection or oral administration of 4-dimethylaminoazobenzene to rats produced liver cirrhosis and cancer, and chronic dermal exposure produced skin cancer. Chronic oral administration of 4-dimethylaminoazobenzene to dogs produced bladder cancer. 4-Dimethylaminoazobenzene has been reported to cause skeletal defects in mice when administered at single doses during embryogenesis and also to cause the production of abnormal sperm in mice.

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• **Signs and symptoms of exposure**

Long-term (chronic): Exposure to 4-dimethylaminoazobenzene can cause contact dermatitis, weakness, dizziness, a feeling of euphoria, shortness of breath, irregular muscular action, and a bluish discoloration of skin and mucous membranes (due to methemoglobinemia).

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-dimethylaminoazobenzene, 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, skin, 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-dimethylaminoazobenzene.

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 skin or 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-dimethylaminoazobenzene. 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, skin, and urinary tract 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 4-dimethylaminoazobenzene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

• **Sentinel health events**

Acute and delayed-onset SHE's include: methymoglobinemia.

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting 4-dimethylaminoazobenzene dust with glass-fiber filters and Gas-Chrom P sorbent followed by elution with 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure 4-dimethylaminoazobenzene may also be used if available. A detailed sampling and analytical method for 4-dimethylaminoazobenzene may be found in the *NIOSH Manual of Analytical Methods* (method number 284).

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-dimethylaminoazobenzene 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 4-dimethylaminoazobenzene 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 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-dimethylaminoazobenzene 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-dimethylaminoazobenzene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 4-dimethylaminoazobenzene'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-dimethylaminoazobenzene 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 1910.1015:

Areas where 4-dimethylaminoazobenzene 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 are 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-dimethylaminoazobenzene, including local and systemic toxicity, the specific nature of the operations 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-dimethylaminoazobenzene which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 4-dimethylaminoazobenzene into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 4-dimethylaminoazobenzene 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-dimethylaminoazobenzene 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-dimethylaminoazobenzene from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 4-dimethylaminoazobenzene 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-dimethylaminoazobenzene

Operations	Controls
During use in research and laboratory facilities; during use as a coloring agent for polishes, waxes, polystyrene, petroleum, and soap	Process enclosure, restricted access, local exhaust ventilation where appropriate, 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-dimethylaminoazobenzene, 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-dimethylaminoazobenzene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 4-dimethylaminoazobenzene 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-dimethylaminoazobenzene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 4-dimethylaminoazobenzene gets on the skin, wash it immediately with soap and water. If 4-dimethylaminoazobenzene 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-dimethylaminoazobenzene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in solid form, 4-dimethylaminoazobenzene may be collected and placed in an appropriate container.
3. 4-Dimethylaminoazobenzene solid or liquid 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-dimethylaminoazobenzene are prohibited by OSHA.
4. For small quantities of liquids containing 4-dimethylaminoazobenzene, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing 4-dimethylaminoazobenzene 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 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-dimethylaminoazobenzene

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 Dimethylaniline

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: $C_6H_5N(CH_3)_2$
- Synonyms: N,N-dimethylaniline
- Appearance and odor: Straw to brown-colored liquid with a characteristic amine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethylaniline is 5 parts of dimethylaniline per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 25 milligrams of dimethylaniline per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethylaniline 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 dimethylaniline 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 dimethylaniline.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethylaniline 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: Dimethylaniline has been shown to cause methemoglobinemia. 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**

Dimethylaniline absorption, whether from inhalation of the vapor or by skin absorption of the liquid, causes anoxia due to the formation of methemoglobin. In dogs, the repeated subcutaneous injection of 1.5 g caused vomiting, weakness, cyanosis, methemoglobinemia, and hyperglobulinemia. It is said to be less toxic than aniline as regards methemoglobin formation but more of a central nervous system depressant. The liquid caused moderate injury in the eye of a rabbit.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 121
2. Boiling point (760 mm Hg): 192.8 C (379 F)
3. Specific gravity (water = 1): 0.96
4. Vapor density (air = 1 at boiling point of dimethylaniline): 4.2
5. Melting point: 2.5 C (36 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):

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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1.6

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. Contact with strong acids may cause violent spattering.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving dimethylaniline.

4. Special precautions: Liquid dimethylaniline will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 62.8 C (145 F) (closed cup)

2. Autoignition temperature: 371 C (700 F)

3. Flammable limits in air, % by volume: Lower: 1.0 (calculated at flash point)

4. Extinguishant: Foam, dry chemical, carbon dioxide

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of dimethylaniline.

2. Eye Irritation Level: Dimethylaniline vapor is not known to be an eye irritant. Grant reports that "in only one instance has it been involved in an ocular disturbance," and in this instance, it is not known if the disturbance should be attributed to the inhalation of phenol, which was also present, or dimethylaniline.

3. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties of dimethylaniline to air concentrations, 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**

Sampling and analyses may be performed by collection of dimethylaniline 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 dimethylaniline may be used. An analytical method for dimethylaniline 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 skin contact with liquid dimethylaniline, where skin contact may occur.

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

• Where exposure of an employee's body to liquid dimethylaniline 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 dimethylaniline should be removed immediately and not reworn until the dimethylaniline is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid dimethylaniline may contact the eyes.

SANITATION

• Skin that becomes contaminated with dimethylaniline should be immediately washed or showered with soap or mild detergent and water to remove any dimethylaniline.

• Eating and smoking should not be permitted in areas where liquid dimethylaniline is handled, processed, or stored.
• Employees who handle liquid dimethylaniline 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 dimethylaniline may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of dye and dye intermediates; synthesis of explosives; pharmaceuticals; polyester resin systems; and intermediates for vanillin	Process enclosure; local exhaust ventilation; personal protective equipment
Use in absorption of sulfur dioxide	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 dimethylaniline 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 liquid dimethylaniline gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid dimethylaniline 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 dimethylaniline, 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 dimethylaniline 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 dimethylaniline 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.
• Waste disposal methods:
Dimethylaniline 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.

ADDITIONAL INFORMATION

To find additional information on dimethylaniline, look up dimethylaniline 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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RESPIRATORY PROTECTION FOR DIMETHYLANILINE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
100 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 100 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 Dimethyl-1,2-Dibromo-2,2-Dichloroethyl 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: $(CH_3O)_2P(O)OCHBrCBrCl_2$ or $C_4H_7Br_2Cl_2O_4P$
- Synonyms: Naled; 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate; Dibrom
- Appearance and odor: Colorless solid or straw-colored liquid with a slightly pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate is 3 milligrams of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate 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**

1. Short-term Exposure: If vapors of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate are inhaled, effects on the respiratory system and the eyes are the first to appear. These include tightness of the chest, wheezing, cough, excessive salivation, nasal discharge, aching in and behind the eyes, blurred vision, tearing, and headache. After swallowing the liquid, intestinal effects include loss of appetite, nausea, vomiting, cramps, and diarrhea. If spilled on the skin, it may cause itching, redness, and irritation. On being absorbed through the skin, this chemical may cause twitching and sweating at the site of absorption. If splashed in the eye, it may cause irritation. Severe intoxication, which may occur from breathing this chemical, swallowing it, or absorbing it through the skin or eye, may cause lightheadedness, slurred speech, muscle twitching, irregular heart beat, convulsions, paralysis, coma, and death.

2. Long-term Exposure: Repeated exposure to levels of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate may make a person more susceptible to the effects of this and related chemicals.

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 dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate 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 skin sensitization to dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, 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 disorders.

—Cholinesterase determination: Dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum

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 erythrocytes should be determined by using medically acceptable biochemical assays prior to any 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 semiannually or at any time overexposure is suspected or signs or symptoms of toxicity occur.

• **Summary of toxicology**

This substance is an anticholinesterase agent; absorption may occur from inhalation of the vapor, by skin absorption, or ingestion of the liquid. Signs and symptoms of overexposure are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine in the nervous system, skeletal and smooth muscles, and secretory glands. The sequence of the development of systemic effects varies with the route of entry. The onset of signs and symptoms occurs promptly, and almost always within 12 hours. After inhalation of the vapor, 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 of the liquid, gastrointestinal effects such as anorexia, nausea, vomiting, abdominal cramps, and diarrhea appear within 15 minutes to 2 hours. After skin absorption of the liquid, 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 enhanced 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, but these are often reversed by the establishment of adequate pulmonary ventilation. In nonfatal cases, complete symptomatic recovery usually occurs within 1 week; increased susceptibility to the effects of anticholinesterase agents persists for long periods 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. Dermatitis occurred on the arms, face, neck, and abdomen of 9 of 12 persons working in a field of flowers which had been freshly sprayed with a solution of Dibrom; three of four workers patch-tested were positive to a 60% solution of Dibrom in xylene and negative to xylene alone. The liquid in the eye is expected to cause injury.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 381
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.97
4. Vapor density (air = 1 at boiling point of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate): Not
5. Melting point: 27 C (81 F)
6. Vapor pressure at 20 C (68 F): 0.0002 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble, decomposes about 10% per day in water
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 bromide, hydrogen chloride, phosphoric acid, and carbon monoxide) may be released when dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate decomposes.
4. Special precautions: Liquid dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Dibrom 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**

At the time of publication of this guideline, no measurement method for dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate 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 skin contact with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, where skin contact may occur.
- If employees' clothing may have become contaminated with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liqcontaining dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which may have become contaminated with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, the person performing the operation should be informed of dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate's hazardous properties.
- Non-impervious clothing which becomes contaminated with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should be removed immediately and not reworn until the dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate 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 dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should be immediately washed or showered with soap or mild detergent and water to remove any dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate.
- Workers subject to skin contact with dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should wash any areas of the body which may have contacted dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate at the end of each work day.
- Eating and smoking should not be permitted in areas where dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate are handled, processed, or stored.
- Employees who handle dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl 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 dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate may occur and control methods which may be effective in each case:

Operation	Controls
Use as an agricultural insecticide and acaricide applied to fruit, vegetables, and agronomic crops; use in domestic, commercial, and agricultural premises	Personal protective equipment
Use in compounding water-base paints and floor polishes for insecticidal properties	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 dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immedi-

ately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate 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 dimethyl-1,2-dibromo-2,2-dichloroethyl 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 dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate 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 dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. If in the solid form, collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate or liquids containing dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal methods:

Dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate may be disposed of:

1. If in the solid form, by disposing in a secured sanitary landfill.
2. If in the liquid form, by absorbing in vermiculite, dry sand, earth, or a similar material, and disposing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR DIMETHYL-1,2-DIBROMO-2,2-DICHLOROETHYL PHOSPHATE

Condition	Minimum Respiratory Protection* Required Above 3 mg/m³
Particulate Concentration	
15 mg/m³ or less	Any dust and mist respirator, except single-use, including pesticide respirators which meet the requirements of this class.
30 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator, including pesticide respirators which meet the requirements of this class. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
150 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.
1800 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 mode.
Greater than 1800 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, 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 Dimethyl Formamide

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: $HCON(CH_3)_2$
- Synonyms: N,N-dimethyl formamide; DMF
- Appearance and odor: Colorless liquid with a faint, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethyl formamide is 10 parts of dimethyl formamide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 30 milligrams of dimethyl formamide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethyl formamide 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 dimethyl formamide or skin contact with dimethyl formamide may cause abdominal distress, colicky abdominal pain, loss of appetite, nausea, vomiting, constipation, diarrhea, facial flushing (especially after drinking alcohol), liver injury, agitation, and increased blood pressure. Skin contact may cause skin irritation.

2. Long-term Exposure: Repeated or prolonged skin contact with dimethyl formamide may cause a 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 dimethyl formamide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethyl formamide 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, kidneys, and cardiovascular system 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 dimethyl formamide, a profile of liver function should be obtained by using 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**

Dimethyl formamide vapor is toxic to the liver. Repeated exposure of rats to concentrations of 100 to 450 ppm for 4 months resulted in necrosis of the liver and mild kidney damage. Animal studies have shown toxic effects at high levels on multiple organ systems. Thirteen workers exposed to concentrations below 20 ppm and occasionally to higher levels for up to 32 weeks complained of nausea, vomiting, and colic; some cases of hepatomegaly were detected. A worker who was splashed with the liquid over 20% of his body surface initially suffered only dermal irritation and hyperemia; abdominal pain began 62 hours after the exposure and became progressively more severe, with vomiting; the blood pressure was elevated to 190/100; the effects gradually subsided and were entirely abated by the 7th day after the exposure. Some workers have noted flushing of the face after inhalation of the vapor, especially with coincident ingestion of alcoholic bever-

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

ages. Effects resemble those of porphyria. Prolonged or repeated skin contact with the liquid may cause dermatitis as a result of a defatting action.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 73.1
2. Boiling point (760 mm Hg): 153 C (307 F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of dimethyl formamide): 2.5
5. Melting point: −61 C (−78 F)
6. Vapor pressure at 20 C (68 F): 2.7 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): 0.17

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 350 C (662 F) may cause decomposition and development of pressure in closed containers.

2. Incompatibilities: Contact with carbon tetrachloride and other halogenated compounds, particularly when in contact with iron, or contact with strong oxidizers may cause fires and explosions. Dimethyl formamide may react vigorously with alkylaluminums when the latter are used as polymerization catalysts.

3. Hazardous decomposition products: Toxic gases and vapors (such as dimethylamine and carbon monoxide) may be released in a fire involving dimethyl formamide.

4. Special precautions: Dimethyl formamide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 58 C (136 F) (closed cup)
2. Autoignition temperature: 445 C (833 F)
3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 15.2 (at 100 C (212 F))
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide. Do not use halogenated extinguishing media.

- **Warning properties**

1. Odor Threshold: According to the Department of Transportation's *Hazardous Chemical Data*, the odor threshold of dimethyl formamide is 100 ppm.

2. Eye Irritation Level: According to Deichmann and Gerarde, dimethyl formamide "is highly irritating to skin, eyes, and mucous membranes." No quantitative information is available concerning the threshold levels of irritation.

3. Evaluation of Warning Properties: Since the odor threshold of dimethyl formamide is 10 times higher than the permissible exposure limit, and since no other quantitative information is available relating to warning properties to air concentrations, 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 dimethyl formamide vapors using a silica gel tube, followed by desorption with methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure dimethyl formamide may be used. An analytical method for dimethyl formamide 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 dimethyl formamide.
- Non-impervious clothing which becomes contaminated with dimethyl formamide should be removed

promptly and not reworn until the dimethyl formamide is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid dimethyl formamide may contact the eyes.

SANITATION

• Skin that becomes contaminated with dimethyl formamide should be promptly washed or showered to remove any dimethyl formamide.

• Employees who handle liquid dimethyl formamide 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 dimethyl formamide may occur and control methods which may be effective in each case:

Operation	Controls
Use as resin and polymer solvent as spinning solvent for acrylic fibers; booster solvent in coating, printing, and adhesive formulations	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate, catalyst and reaction medium in chemical manufacturing industry	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a selective absorption and extraction solvent for recovery, purification absorption, separation and desulfurization of non-paraffinics from paraffin hydrocarbons	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of paint stripper component for removal of vinyl films, epoxy coatings, and varnish finishes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in pigment and dye industry to improve dyeing properties; use as solvent of dyes and pigments for use with textiles, wood, leather, films, paper, and plastics; use as a crystallization solvent in pharmaceutical industry; use as a solvent for carbonaceous deposit cleaning	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous applications for high-voltage capacitors, oil sludge dispersing agent, antistall gasoline additive, quench for tinned parts and wood pulping	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 dimethyl formamide 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 dimethyl formamide gets on the skin, promptly flush the contaminated skin with water. If liquid dimethyl formamide soaks through the clothing, remove the clothing promptly and flush the skin with water. Get medical attention promptly.

• **Breathing**

If a person breathes in large amounts of dimethyl formamide, 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 dimethyl formamide 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 some-

one 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 dimethyl formamide 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. Dimethyl formamide 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 dimethyl formamide vapors are permitted.

• Waste disposal methods:

Dimethyl formamide 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 DIMETHYL FORMAMIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
100 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
500 ppm or less	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.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of dimethyl formamide; 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 3500 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 1,1-DIMETHYLHYDRAZINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 1,1-dimethylhydrazine 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:** $C_2N_2H_8$
- **Structure:** $(CH_3)_2N\text{-}NH_2$
- **Synonyms:** Asymmetric dimethylhydrazine; dimazine; dimethylhydrazine; N,N-dimethylhydrazine; dimethylhydrazine unsymmetrical; DMH; UDMH
- **Identifiers:** CAS 157-14-7; RTECS MV2450000; DOT 1163, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid that fumes in air, gradually turns yellow, and has a fishy or ammonialike odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 60.12
2. Boiling point (at 760 mmHg): 63.9°C (147°F)
3. Specific gravity (water = 1): 0.782
4. Vapor density (air = 1 at boiling point of 1,1-dimethylhydrazine): 2.08
5. Melting point: -58°C (-72°F)
6. Vapor pressure at 25°C (77°F): 156.8 mmHg
7. Miscible with water
8. Evaporation rate (butyl acetate = 1): 8.6
9. Saturation concentration in air (approximate) at 25°C (77°F): 20.6% (206,000 ppm)
10. Ionization potential: 7.46 eV

- **Reactivity**

1. Incompatibilities: 1,1-dimethylhydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving 1,1-dimethylhydrazine.
3. Caution: 1, 1-Dimethylhydrazine will attack cork, some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -15°C (5°F) (closed cup)
2. Autoignition temperature: 249°C (480°F)
3. Flammable limits in air, % by volume: Lower, 2; Upper, 95
4. Extinguishant: Alcohol foam, dry chemical, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Caution: 1,1-dimethylhydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

1. Odor threshold: 6-14 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 1,1-dimethylhydrazine is 0.5 parts of 1,1-dimethylhydrazine per million parts of air (ppm) [1 milligram of 1,1-dimethylhydrazine 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 the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that 1,1-dimethylhydrazine 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 0.06 ppm (0.15 mg/m^3) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Con-

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ference of Governmental Industrial Hygienists (ACGIH) has designated 1,1-dimethylhydrazine as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 0.5 ppm (1.0 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for 1, 1-dimethylhydrazine

	Exposure limits ppm	mg/m³
OSHA PEL TWA (Skin)*	0.5	1
NIOSH REL (Ca)† Ceiling (120 min)	0.06	0.15
ACGIH TLV® TWA (Skin) (A2)§	0.5	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.
§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

1,1-Dimethylhydrazine 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 1,1-dimethylhydrazine by mice, rats, or dogs caused central nervous system (CNS) stimulation, respiratory distress, convulsions, and death. Repeated daily exposure of dogs to 1,1-dimethylhydrazine vapor produced CNS depression, salivation, vomiting, diarrhea, loss of muscular coordination (ataxia), convulsive seizures, and hemolytic anemia. Chronic oral administration of 1,1-dimethylhydrazine to mice caused tumors of the blood vessels, lungs, kidneys, and liver.
2. *Effects on humans:* Exposure of workers to 1,1-dimethylhydrazine has caused increased blood pressure, fatty infiltration of the liver, impaired liver function (resulting in elevated serum glutamic-pyruvic transaminase levels, respiratory distress, hemolysis, and reduced oxygen supply to tissues (anoxia).

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure can cause a choking sensation, chest pain, breathing difficulty (dyspnea), lethargy, nausea, vomiting, and irritation of the skin, eyes, nose, and throat.
2. *Long-term (chronic):* Exposure to 1,1-dimethylhydrazine can cause pulmonary irritation, conjunctivitis, and gastrointestinal 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 1,1-dimethylhydrazine, 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, red blood cells, 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). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis. 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 1,1-dimethylhydrazine 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. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to 1,1-dimethylhydrazine.

• 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 1,1-dimethylhydrazine. 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, kidneys, red blood cells, 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. Because occupational exposure to 1,1-dimethylhydrazine 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 1,1-dimethylhydrazine. 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 120-minute sample or a series of consecutive samples that total 120 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 1,1-dimethylhydrazine vapors with sulfuric acid-coated silica gel tubes and analyzing by gas chromatography. Direct-reading devices calibrated to measure 1,1-dimethylhydrazine may also be used if available. A detailed sampling and analytical method for 1,1-dimethylhydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

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 1,1-dimethylhydrazine.

SANITATION

Clothing which is contaminated with 1,1-dimethylhydrazine 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 1,1-dimethylhydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 1,1-dimethylhydrazine'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 1,1-dimethylhydrazine 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 1,1-dimethylhydrazine 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 1,1-dimethylhydrazine 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 1, 1-dimethylhydrazine

Operations	Controls
During the formulation of and use in jet and rocket propellants	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture of 1,1-dimethylhydrazine and during maintenance of manufacturing and storage equipment	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the chemical synthesis of catalysts, automotive antifreeze, pharmaceuticals, dyestuffs, and stabilizing agents	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the formulation of photographic developers and the processing of styrene-butadiene rubber	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 1,1-dimethylhydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 1,1-dimethylhydrazine 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 1,1-dimethylhydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 1,1-dimethylhydrazine gets on the skin, wash it immediately with soap and water. If 1,1-dimethylhydrazine 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 1,1-dimethylhydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing 1,1-dimethylhydrazine may be flushed with water and collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing 1,1-dimethylhydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. 1,1-Dimethylhydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

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 1, 1-dimethylhydrazine

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 Dimethylphthalate

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: $C_{10}H_{10}O_4$
- Synonyms: DMP
- Appearance and odor: Colorless, oily liquid with a slight ester odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethylphthalate is 5 milligrams of dimethylphthalate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethylphthalate can affect the body if it is swallowed, is inhaled, or comes in contact with the eyes.

- **Effects of overexposure**

Overexposure to hot vapors or mists of dimethylphthalate may cause irritation of the nasal passages and the mouth and throat. Eye contact with liquid dimethylphthalate causes pain. If swallowed, dimethylphthalate may cause irritation of the stomach, dizziness, and unconsciousness.

- **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 dimethylphthalate.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to dimethylphthalate at potentially hazardous levels.

- **Summary of toxicology**

Extensive experience with dimethylphthalate as an insect repellent has shown that it is relatively nonirritating to the skin, eyes, and mucous membranes. Aerosols from heated dimethylphthalate may cause irritation of the eyes and upper respiratory tract. In one fatal case of suicidal ingestion of a mixture containing dimethylphthalate and ketone peroxides, the principal toxic symptoms were marked esophagitis and gastritis with hemorrhage. Animal experiments to determine dermal and oral toxicity of dimethylphthalate showed that extremely high doses were considered necessary to produce toxic effects. Dimethylphthalate was found to be teratogenic by intraperitoneal injection of doses representing 1/10, 1/5, 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: 194
2. Boiling point (760 mm Hg): 285 C (545 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of dimethylphthalate): 6.7
5. Melting point: 0 to 2 C (32 to 36 F)
6. Vapor pressure at 100.3 C (212 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.04
8. Evaporation rate (methyl 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 dimethylphthalate.

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

4. Special precautions: None

- **Flammability**

1. Flash point: 146 C (295 F) (closed cup)
2. Autoignition temperature: 556 C (1032 F)
3. Flammable limits in air, % by volume: Lower: 1.2 (calculated at flash point)
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

According to Grant, contact of dimethylphthalate with the eye "produces considerable pain, but causes either no damage or only slight reversible disturbance of the epithelium." Air concentrations which would produce this effect 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**

At the time of publication of this guideline, no measurement method for dimethylphthalate 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 splash-proof safety goggles where liquid dimethylphthalate may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dimethylphthalate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a plasticizer in compounding of plastics, primarily cellulose acetate, nitrocellulose, ethylcellulose, cellulose acetate butyrate, polystyrene, polyvinyl acetate, polyvinyl butyral, and polyvinyl chloride	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of surface coatings containing plasticized resins and polymers, including furniture lacquers, printing inks, textile and paper coatings, and moisture-proof coatings for cellophane	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during molding, casting, extrusion, or other processing of heated, plasticized resins and polymers in manufacture of plastic articles	Local exhaust ventilation; general dilution ventilation
Use in spray (or dip applications or any method involving heat) of surface coatings containing plasticized resins and polymers, including furniture lacquers, printing inks, textiles and paper coatings, and moisture-proof coatings on cellophane	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a plasticizer in compounding of nitrile and neoprene rubber and chlorinated rubber	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in spray or other applications of adhesives containing plasticizer, including polyvinyl acetate adhesives for cellulose acetate films, covering cut-out windows in cartons, or laminating cellulose acetate film to paper	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during processing of heated plasticized nitrile, neoprene, and chlorinated rubber into manufactured articles	Local exhaust ventilation; general dilution ventilation
Use during preparation of adhesives containing plasticizer, including polyvinyl acetate adhesives for cellulose film	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of insect repellant formulations	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 dimethylphthalate 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 dimethylphthalate saturates the clothing, remove and clean the clothing before wearing it again. Wash any dimethylphthalate 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 dimethylphthalate, 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 dimethylphthalate 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 dimethylphthalate 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:

Dimethylphthalate 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.

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RESPIRATORY PROTECTION FOR DIMETHYLPHTHALATE

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 Health Guideline for Dimethylsulfate

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: $(CH_3)_2SO_4$
- Synonyms: Methyl sulfate
- Appearance and odor: Colorless, oily liquid with a faint onion odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dimethylsulfate is 1 part of dimethylsulfate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of dimethylsulfate per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for dimethylsulfate a Threshold Limit Value of 0.1 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dimethylsulfate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may readily enter the body through the skin.

- **Effects of overexposure**

Dimethylsulfate vapor is an extremely severe irritant of the eyes, respiratory tract, and skin. While exposure often produces no immediate effects other than slight eye and nose irritation, after a period of up to 10 hours or more, headache and giddiness with intense pain on exposure to light may occur. This is usually followed by inflammation of the throat and voice box, difficulty in speaking, difficulty in swallowing, cough, tightness of the chest, shortness of breath, a blue coloration of the skin, vomiting, diarrhea, and painful urination. Other effects are delirium, fever, yellow jaundice, and bloody urine. Liver and kidney damage may occur. If the liquid is swallowed, in addition to causing burns of the throat and stomach, the above effects may occur. Contact of the liquid with the eyes and skin will cause severe burns. Animal experiments have shown that this chemical may cause cancer in animals and their offspring.

- **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 dimethylsulfate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dimethylsulfate 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 eyes, respiratory tract, liver, kidneys, and central nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to dimethylsulfate, a urinalysis 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 dimethylsulfate, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—14" x 17" chest roentgenogram: Dimethylsulfate causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Dimethylsulfate is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance 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.

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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.

• **Summary of toxicology**

Dimethylsulfate vapor is an extremely severe irritant of the eyes, mucous membranes, and skin; it is carcinogenic in rats. It has a strong vesicant action and rapidly hydrolyzes in the presence of water to produce sulfuric acid and methanol. It caused malignant tumors in rats in various organs by inhalation, subcutaneous injection, and following prenatal exposure. A single intravenous dose of 20 mg/kg given to 8 pregnant rats on day 15 of gestation induced malignant tumors, including 3 tumors of the nervous system, in 7 of 59 offspring which were observed for over 1 year. The LC50 in rats was 75 ppm for 18 minutes; autopsy findings were marked pulmonary edema, pulmonary emphysema, peribronchitis, and focal necrosis of the liver. Several human deaths have occurred from occupational exposure. While exposure of humans often produces no immediate effects other than occasional slight eye and nose irritation, after a latent period of up to 10 hours or more, there is onset of headache and giddiness with intense conjunctival irritation, photophobia, and periorbital edema; this is usually followed by inflammation of the pharyngo-laryngeal mucosa, dysphonia, aphonia, dysphagia, productive cough, oppression in the chest, dyspnea and cyanosis; vomiting and diarrhea may intervene. Dysuria may occur for 3 to 4 days; there may be persistence of laryngeal edema for up to 2 weeks and of photophobia for several months. Other effects are delirium, fever, icterus, albuminuria, and hematuria. Contact of the liquid with the eyes or skin will cause very severe burns due to its powerful vesicant action. In one incident of moderate skin contact with the liquid, generalized intoxication occurred even though there was prompt treatment of the skin; the vapor was inhaled for no more than a few minutes.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 126.1
2. Boiling point (760 mm Hg): 188.8 C (372 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of dimethylsulfate): 4.35
5. Melting point: −31.8 C (−25 F)
6. Vapor pressure at 20 C (68 F): 0.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 2.8 (reacts slowly)
8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Contact with water may allow formation of flammable concentrations of methyl alcohol.
2. Incompatibilities: Contact with strong oxidizers or with strong ammonia solutions may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfuric acid mist, methyl alcohol, and carbon monoxide) may be released in a fire involving dimethylsulfate.
4. Special precautions: Dimethylsulfate will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 83.3 C (182 F) (closed cup)
2. Autoignition temperature: 187.8 C (370 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: Patty states that "dimethylsulfate is a colorless, oily liquid, which is nearly odorless or which may have a faint onion-like odor."
2. Irritation Levels: Grant states that "injury of the eye by vapor of dimethylsulfate is a much more common industrial accident than injury by a splash of liquid, which is more easily prevented by goggles. Numerous instances of burns and poisoning from the vapor have been described. Also, in animal eyes the effects of the vapor have several times been studied and reproduced. Characteristically, during exposure to vapor of dimethylsulfate the patient or experimental animal is not aware of irritation or unpleasant sensation but begins to develop discomfort several hours later.

'Moeschlin in his book on poisonings particularly has placed great emphasis on the latent period that is characteristic of the action of dimethylsulfate vapors on the eyes, giving description of specific cases in which there were latent periods as long as six hours before severe inflammation of the eyes and respiratory tract developed. Browning in her book on toxicology has reviewed several of the reports in the literature of eye involvement from vapor exposure.

'Typical industrial exposure occurs when workmen pour dimethylsulfate from one container to another, with no irritation of eyes or nose, or no unpleasant odor to warn of danger. After several hours the eyes begin to feel irritated and have a sandy sensation. Photophobia and lacrimation develop; the lids become edematous and the conjunctiva hyperemic. The skin of the face and other exposed parts is reddened. The symptoms increase in intensity for several hours, and then superficial clouding and irregularity of the corneal epithelium may be seen. Associated with the ocular symptoms are temporary loss of smell and taste, with hoarseness and irritation of the respiratory passages which may become severe, and in the worst cases may develop into fatal pneumonia.

'The course of the eye injuries in the mildest cases may be spontaneous return to normal in a few days, or, in severe cases, gray necrosis of the epithelium, edema and infiltration of the corneal stroma, and permanent

partial opacification may result."

No quantitative information is available concerning the levels of dimethylsulfate which produce eye irritation. The effects on the eyes are delayed.

3. Evaluation of Warning Properties: Since dimethylsulfate is "almost odorless," and since the irritant effects produced by this compound are delayed, dimethylsulfate 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 dimethylsulfate 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 dimethylsulfate.

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

• Where there is any possibility of exposure of an employee's body to liquid dimethylsulfate, 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 dimethylsulfate should be removed immediately and not reworn until the dimethylsulfate 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 dimethylsulfate contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid dimethylsulfate, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with dimethylsulfate should be immediately washed or showered with soap or mild detergent and water to remove any dimethylsulfate.

• Employees who handle liquid dimethylsulfate 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 dimethylsulfate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a methylating agent in organic chemical industry for manufacture of esters, ethers, and amines	Enclosed system/ segregation; general dilution ventilation; personal protective equipment
Use in manufacture of dyes, dyestuffs, coloring agents, and perfumes; use in pharmaceutical industry as a solvent for separation/preparation of mineral oils	Enclosed system/ segregation; general dilution ventilation; personal protective equipment
Use during analysis of automobile fluids	Enclosed system/ segregation; 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 dimethylsulfate or strong concentrations of dimethylsulfate vapors 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 dimethylsulfate or strong concentrations of dimethylsulfate vapors get on the skin, immediately flush the contaminated skin with large amounts of water. If liquid dimethylsulfate or strong concentrations of dimethylsulfate vapors 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 dimethylsulfate, 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 dimethylsulfate has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the dimethylsulfate. 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, 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 dimethylsulfate is spilled or leaked, the following steps should be taken:

1. 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:

Dimethylsulfate 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.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Dimethylsulfate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.

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• International Agency for Research on Cancer: *Some Aromatic Amines, Hydrazine and Related Substances, N-Nitroso Compounds and Miscellaneous Alkylating Agents*, Vol. 4 of *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man*, Lyon, France, 1974.

• Manufacturing Chemists Association, Inc.: *Chemical Safety Data Sheet SD-19, Dimethylsulfate*, Washington, D.C., 1966.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Spector, W. S. (Vols. I, II), Negherbon, W. O. (Vol. III), Grebe, R. M. (Vol. IV), and Dittmer, D. S. (Vol. V) (eds.): *Handbook of Toxicology*, Saunders, Philadel-

* 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 4, 1974.

RESPIRATORY PROTECTION FOR DIMETHYLSULFATE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
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 with a full facepiece providing protection against dimethylsulfate. Any escape self-contained breathing apparatus with a full facepiece.

*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 dimethylsulfate; 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 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DINITOLMIDE

INTRODUCTION

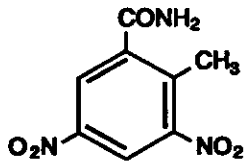
This guideline summarizes pertinent information about dinitolmide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations 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**

  $C_8H_7N_3O_5$

- **Structure**



- **Synonyms**

  Zoalene; 2-methyl-3,5-dinitrobenzamide; Coccidine A; Coccidot; dinitolmid; Zoamix; 3,5-dinitro-o-toluamide

- **Identifiers**

  1. CAS No.: 148-01-6
  2. RTECS No.: XS4200000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Dinitolmide is a noncombustible, yellowish, crystalline solid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 225.2
  2. Boiling point: Data not available
  3. Specific gravity: Data not available
  4. Vapor density: Data not available
  5. Melting point: 177°C (350.6°F)
  6. Vapor pressure: Data not available

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7. Solubility: Very slightly soluble in water; soluble in acetone, acetonitrile, dioxane, and dimethylformamide.

8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: None reported

3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving dinitolmide.

4. Special precautions: None reported.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating for dinitolmide; 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 dinitolmide 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 dinitolmide.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dinitolmide [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 for dinitolmide [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dinitolmide 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 and ACGIH limits are based on the risk of liver damage associated with exposure to dinitolmide [NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to dinitolmide causes methemoglobinemia and liver changes in animals. The oral LD_{50} in rats is 600 mg/kg [NIOSH 1993]. Rats given a single 150-mg/kg oral dose of dinitolmide developed methemoglobinemia [Gosselin et al. 1984]. Rats fed 6 mg/kg dinitolmide daily for 2 years showed slightly increased liver weights and fatty liver changes in both sexes at autopsy [ACGIH 1991]. Rats fed 3 mg/kg/day showed no adverse effects on growth, mortality rate, tumor incidence, fertility, gestation, or viability [ACGIH 1991]. Beagle dogs fed 10 mg/kg/day for 1 year also showed no effects when evaluated on these measures [ACGIH 1991]. Dinitolmide is mutagenic in bacterial test systems [NIOSH 1993].

2. *Effects on Humans:* In contact with the skin, dinitolmide has caused allergic contact dermatitis in two female poultry attendants [ACGIH 1991]. No other reports on dinitolmide's effects in humans are available.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to dinitolmide have been reported in humans.

2. *Chronic exposure:* Chronic exposure to dinitolmide may cause allergic contact dermatitis. The signs and symptoms include redness, itching, and swelling (hives).

- **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 dinitolmide 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 dinitolmide and lead to worker exposures to this substance:

—Use as a coccidiostat and food additive

The following methods are effective in controlling worker exposures to dinitolmide, 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 dinitolmide, 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 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 dinitolmide 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 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 dinitolmide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dinitolmide on the skin 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. No biological monitoring test acceptable for routine use has yet been developed for dinitolmide.

- **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 dinitolmide is made using a 37-mm glass fiber filter. 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 high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Laboratory In-House Methods File [ACGIH 1991].

PERSONAL HYGIENE

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

Clothing contaminated with dinitolmide should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles dinitolmide 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 dinitolmide or a solution containing dinitolmide is handled, processed, or stored.

STORAGE

Dinitolmide 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 dinitolmide 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 dinitolmide, 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:

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**

  Dinitolmide 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 dinitolmide; 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 dinitolmide 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 dinitolmide 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 dinitolmide 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 and gloves should be worn to prevent skin contact with dinitolmide. 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 dinitolmide 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 dinitolmide.

If dinitolmide 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 dinitolmide might contact the eyes (e.g., through dust particles). Eyewash fountains should be available within the immediate work area whenever the potential exists for eye contact with dinitolmide.

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Occupational Health Guideline for Dinitrobenzene (All 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: Ortho: 1,2-$C_6H_4(NO_2)_2$; Meta: 1,3-$C_6H_4(NO_2)_2$; Para: 1,4-$C_6H_4(NO_2)_2$
- Synonyms: O-dinitrobenzene; 1,2-dinitrobenzene; m-dinitrobenzene; 1,3-dinitrobenzene; p-dinitrobenzene; 1,4-dinitrobenzene
- Appearance: Pale yellow solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dinitrobenzene is 1 milligram of dinitrobenzene per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for dinitrobenzene a Threshold Limit Value of 0.15 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dinitrobenzene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It is readily absorbed through the skin, either as solid, liquid, or vapor. Even a small amount absorbed from clothes or shoes may cause toxic symptoms.

- **Effects of overexposure**

Dinitrobenzene may affect the ability of blood to carry oxygen. A bluish discoloration of the skin may occur with headache, irritability, dizziness, weakness, nausea, vomiting, shortness of breath, drowsiness, and unconsciousness. If treatment is not given promptly, death may occur. The onset of symptoms may be delayed. Consuming alcohol may make symptoms worse. Dinitrobenzene may also cause an unpleasant taste or burning sensation in the mouth, dry, throat, and thirst. The eyes, hair, and skin may become yellowish. Dinitrobenzene may cause reduced vision. In addition, liver damage may occur. Repeated or prolonged exposure to dinitrobenzene may cause anemia.

- **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 dinitrobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dinitrobenzene 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, liver, cardiovascular system, and eyes should be stressed.

—A complete blood count: Dinitrobenzene has been shown to cause methemoglobinemia. Those with blood disorders may be at increased risk. 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. Observe for Heinz bodies.

—Liver function tests: Since liver damage has been observed in humans exposed to dinitrobenzene, a profile of liver function should be performed by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Absorption of any isomer of dinitrobenzene, whether from inhalation of the vapor or dust or skin absorption

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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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of the solid, causes anoxia due to the formation of methemoglobin; chronic exposure produces anemia. Exposed workers have complained of an unpleasant taste, burning sensation in the mouth, dry throat, and thirst. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and is often recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. Until the methemoglobin concentration approaches approximately 40%, the individual may feel well, have no complaints, and may insist nothing is wrong. At methemoglobin concentrations of over 40%, there usually is weakness and dizziness; up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. The ingestion of alcohol has been reported to aggravate the toxic effects of dinitrobenzene. Chronic exposure of workers causes anemia; there are scattered reports of liver injury. Visual impairment has been reported in the form of reduced visual acuity and central scotomas, particularly for red and green colors; yellow discoloration of the conjunctiva and sclera is common. Yellow-brown discoloration of the hair and exposed skin of workers has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 168.1
2. Boiling point (760 mm Hg): Ortho: 318 C (604 F); Meta: 300 C (572 F); Para: 297 C (566 F)
3. Specific gravity (water = 1): Ortho: 1.59; Meta: 1.57; Para: 1.63
4. Vapor density (air = 1 at boiling point of dinitrobenzene): 5.8
5. Melting point: Ortho: 117 C (243 F); Meta: 90 C (194 F); Para: 173 C (343 F)
6. Vapor pressure at 20 C (68 F): All isomers: Much less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 0.01; Meta: 0.05; Para: 0.01
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Dinitrobenzene may detonate when subject to shock or when heated under confinement.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with caustics and metals such as tin and zinc may cause evolution of heat and increase in pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving dinitrobenzene.
4. Special precautions: Liquid dinitrobenzene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Explodes
2. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): Greater than 100 centimeters
2. Autoignition temperature: Data not available
4. Flammable limits in air, % by volume: Data not available
5. Extinguishant: None

- **Warning properties**

Grant states that "surface contact (with dinitrobenzene) may cause yellowing of the skin, and purportedly of the conjunctiva and cornea, but no original observations on corneal changes were found in the literature." According to Grant, "2,4-dinitrobenzene caused no inflammatory response when this substance was brought into contact with the uveal tract, retina, or conjunctiva" of guinea pigs.

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 dinitrobenzene 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 skin contact with dinitrobenzene or liquids containing dinitrobenzene, where skin contact may occur.

• If employees' clothing may have become contaminated with solid dinitrobenzene, employees should change into uncontaminated clothing before leaving the work premises.

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

• Where exposure of an employee's body to liquids containing dinitrobenzene 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 wet with liquids containing dinitrobenzene should be removed immediately and non-impervious clothing which becomes contaminated with dinitrobenzene should be removed promptly and such clothing should not be reworn until the dinitrobenzene is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where dinitrobenzene or liquids containing dinitrobenzene may contact the eyes.

SANITATION

• Skin that becomes wet with liquids containing dinitrobenzene should be immediately washed or showered with soap or mild detergent and water to remove any dinitrobenzene.

• Skin that becomes contaminated with dinitrobenzene should be promptly washed or showered with soap or mild detergent and water to remove any dinitrobenzene.

• Workers subject to skin contact with dinitrobenzene should wash with soap or mild detergent and water any areas of the body which may have contacted dinitrobenzene at the end of each work day.

• Eating and smoking should not be permitted in areas where dinitrobenzene or liquids containing dinitrobenzene are handled, processed, or stored.

• Employees who handle dinitrobenzene or liquids containing dinitrobenzene 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 dinitrobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of dyes and dye intermediates; use in organic synthesis in chemical industry as photographic developers, and as explosives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in plastics industry as a substitute for camphor in production of celluloid; as a polymerization inhibitor	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an explosive by substituting for TNT; use in explosive shells	Material substitution

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 dinitrobenzene or liquids containing dinitrobenzene 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 dinitrobenzene or liquids containing dinitrobenzene get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If dinitrobenzene or liquids containing dinitrobenzene penetrate 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 dinitrobenzene, 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 dinitrobenzene or liquids containing dinitroben-

zene 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 dinitrobenzene is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities, sweep onto paper or other suitable material and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities may be reclaimed; however, if this is not practical, dissolve in fuel oil and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

Dinitrobenzene may be disposed of:

1. By making packages of dinitrobenzene in paper or other flammable material and burning in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device.
2. By dissolving dinitrobenzene in fuel oil and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DINITROBENZENE (ALL ISOMERS)

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any dust and mist respirator, except single-use.
10 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.
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.
200 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 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.
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.

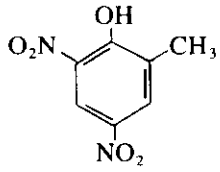
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DINITRO-ORTHO-CRESOL

INTRODUCTION

This guideline summarizes pertinent information about dinitro-ortho-cresol (DNOC) 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:** $C_7H_6N_2O_5$
- **Structure:**



- **Synonyms:** DNOC; 2,4-dinitro-o-cresol; 4,6-dinitro-o-cresol; 3,5-dinitro-2-hydroxytoluene; 4,6-dinitro-2-methyl phenol; antinonin; capsine; chemsect DNOC
- **Identifiers:** CAS 534-52-1; RTECS GO9625000; DOT 2446, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Yellow, odorless solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical Data**

1. Molecular weight: 198.13
2. Boiling point (at 760 mmHg): 312°C (595°F)
3. Vapor density (air = 1 at boiling point of DNOC): 6.8
4. Melting point: 85.8°C (186°F)
5. Vapor pressure at 20°C (68°F): 5.2 x 10^{-5} mmHg
6. Solubility in water, g/100 g water at 20°C (68°F): 0.01

- **Reactivity**

1. Incompatibilities: Heat and strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving DNOC.
3. Caution: DNOC is a combustible solid; DNOC dust may form explosive mixtures with air.

- **Flammability**

1. Minimum explosive dust concentration: 30 g/m³
2. Minimum dust cloud ignition temperature: 340°C (644°F)
3. Extinguishant: Foam, dry chemical, or carbon dioxide

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, DNOC should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for DNOC is 0.2 milligram of DNOC 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) recommended exposure limit (REL) is 0.2 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 0.2 mg/m³ (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for DNOC

	Exposure limits mg/m³
OSHA PEL TWA (Skin)*	0.2
NIOSH REL TWA	0.2
ACGIH TLV® TWA (Skin)	0.2

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

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Division of Standards Development and Technology Transfer

• **Summary of toxicology**

1. *Effects on animals:* Acute inhalation of DNOC by cats produced increased white blood cell counts, decreased red blood cell counts, and decreased blood enzyme activities. Oral administration of DNOC to sheep caused toxic effects to the liver and kidneys. In mutagenicity tests, DNOC caused chromosome damage in the reproductive cells of male mice and DNA damage in bacteria.
2. *Effects on humans:* DNOC has caused increased metabolism, liver and kidney damage, brain hemmorhage with partial loss of circulation, and destruction of nerve sheaths. Chronic ingestion of therapeutic doses of DNOC has produced glaucoma and bilateral cataracts. The toxicity of DNOC is cumulative, and excretion is slow.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to DNOC can cause euphoria, headache, fatigue, nausea, flushed skin, jaundice, muscular incoordination, cough, fever, profuse sweating, excessive thirst, rapid respiration and heart rate, collapse, and coma. Irritation of the skin and eyes can also occur.
2. *Long-term (chronic):* Exposure to DNOC can cause restlessness, anxiety, weight loss, and jaundice.

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 DNOC, 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 endocrine systems (with particular attention to the thyroid gland).

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 DNOC 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 cataracts or chronic diseases of the skin or liver.

• **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 DNOC. 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 nervous and endocrine systems (with particular attention to the thyroid gland) 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 DNOC 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: Cataracts.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to DNOC 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 aver-

age 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 DNOC with cellulose ester membrane filters followed by extraction with ethylene glycol and analysis by high pressure liquid chromatography. Detector tubes or other direct-reading devices calibrated to measure DNOC may also be used if available. A detailed sampling and analytical method for DNOC may be found in the *NIOSH Manual of Analytical Methods* (method number S166).

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 DNOC.

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

SANITATION

Clothing which is contaminated with DNOC 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 DNOC from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DNOC's hazardous properties.

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

Skin that becomes contaminated with DNOC 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 DNOC 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 DNOC 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 DNOC

Operations	Controls
During the manufacture and processing of DNOC	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During cleaning and maintenance of storage vessels	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a herbicide, insecticide, or fungicide	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 DNOC, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DNOC 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 DNOC, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DNOC gets on the skin, wash it immediately with soap and water. If DNOC 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 DNOC 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 DNOC, 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 DNOC vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing DNOC may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. DNOC should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in solid form, DNOC may be collected and placed in an appropriate container.
6. DNOC 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 dinitro-ortho-cresol

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 2 mg/m³	Any dust and mist respirator with a full facepiece
Less than or equal to 5 mg/m³	Any powered air-purifying respirator with a dust and mist filter (substance causes eye irritation or damage—eye protection needed)
	Any supplied-air respirator operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	Any supplied-air respirator with a full facepiece
	Any self-contained breathing apparatus with a full facepiece
Planned or emergency entry into environments containing unknown concentrations or levels above 5 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 0.2 mg/m³ (TWA).

Occupational Health Guideline for Dinitrotoluene

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: $2,4\text{-}(NO_2)_2C_6H_3CH_3$
- Synonyms: 2,4-Dinitrotoluene; DNT
- Appearance and odor: Orange-yellow solid (sometimes shipped molten in tank cars) with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dinitrotoluene is 1.5 milligrams of dinitrotoluene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dinitrotoluene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed; It is readily absorbed through the skin. Even a small amount absorbed from clothes or shoes may cause toxic symptoms.

- **Effects of overexposure**

1. Short-term Exposure: Dinitrotoluene affects the ability of blood to carry oxygen normally. A bluish discoloration of the skin may occur with headache, irritability, dizziness, weakness, nausea, vomiting, shortness of breath, drowsiness, and unconsciousness. If treatment is not given promptly, death may occur. The onset of symptoms may be delayed. The ingestion of alcohol may cause increased susceptibility to the effects of dinitrotoluene.

2. Long-term Exposure: Repeated or prolonged exposure to dinitrotoluene may cause anemia and jaundice.

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 dinitrotoluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dinitrotoluene 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, liver, and cardiovascular system should be stressed.

—A complete blood count: Dinitrotoluene has been shown to cause methemoglobinemia. Those with blood disorders may be at increased risk. 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. Observe for Heinz bodies.

—Liver function tests: Since liver damage has been observed in humans exposed to dinitrotoluene, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur. The level of dinitrotoluene in the urine should be determined; excretion of dinitrotoluene in excess of 25 mg/liter indicates significant absorption.

- **Summary of toxicology**

Dinitrotoluene absorption, whether from inhalation of the vapor or absorption of the solid through skin, causes anoxia due to the formation of methemoglobin; jaundice and anemia have been reported. Signs and symptoms 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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overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious, and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and is often recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. The individual may feel well, have no complaints, and may insist that nothing is wrong until the methemoglobin concentrations approaches approximately 40%. At methemoglobin concentrations of over 40% there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. Ingestion of alcohol is reported to aggravate the toxic effects of dinitrotoluene.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 182.1
2. Boiling point (760 mm Hg): Slow decompostion at 250 C (482 F); self-sustained decomposition at 270 C (518 F)
3. Specific gravity (water = 1): Solid: 1.52; Liquid: 1.32
4. Vapor density (air = 1 at boiling point of dinitrotoluene): Not applicable (too high boiling)
5. Melting point: 70 C (158 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): 0.03
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 250 C (482 F)
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with caustics and chemically active metals such as tin or zinc may cause evolution of heat and increase in pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving dinitrotoluene.
4. Special precautions: Liquid dinitrotoluene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 206.7 C (404 F) (closed cup)
2. Autoignition temperature: Data not available
3. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): Greater than 100 centimeters
4. Flammable limits in air, % by volume: Not available
4. Extinguishant: Water, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of dinitrotoluene.
2. Eye Irritation Level: Grant states that "a severe burn of the skin, eyelids, and cornea of one eye, with permanent scarring, has been attributed in one instance to hot fumes of dinitrotoluene." There is no quantitative information available concerning the concentrations which would produce these effects.
3. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties of dinitrotoluene to air concentration, 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 dinitrotoluene 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 molten dinitrotoluene.
- 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 dinitrotoluene or liquids containing dinitrotoluene, where skin contact may occur.
- If employees' clothing may have become contaminated with solid dinitrotoluene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with dinitrotoluene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dinitrotoluene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dinitrotoluene, the person performing the operation should be informed of dinitrotoluene's hazardous properties.
- Where exposure of an employee's body to dinitrotoluene or liquids containing dinitrotoluene 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 wet with molten dinitrotoluene or liquids containing dinitrotoluene should be removed immediately and non-impervious clothing which becomes contaminated with solid dinitrotoluene should be removed promptly and such clothing should not be reworn until the dinitrotoluene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten dinitrotoluene contacting the eyes.

SANITATION

- Skin that becomes wet with molten dinitrotoluene or liquids containing dinitrotoluene should be immediately washed or showered with soap or mild detergent and water to remove any dinitrotoluene.
- Workers subject to skin contact with dinitrotoluene or liquids containing dinitrotoluene should wash with soap or mild detergent and water any areas of the body which may have contacted dinitrotoluene at the end of each work day.
- Skin that becomes contaminated with dinitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any dinitrotoluene.
- Eating and smoking should not be permitted in areas where dinitrotoluene or liquids containing dinitrotoluene are handled, processed, or stored.
- Employees who handle dinitrotoluene or liquids containing dinitrotoluene 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 dinitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of toluene diisocyanate for production of polyurethane plastics	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in production of military and some commercial explosives; use to plasticize cellulose nitrate in explosives; use to moderate burning rate of propellants and explosives; use in manufacture of gelatin explosives (less sensitive to shock or friction); use as a waterproofing coating for some smokeless powders; use as an intermediate in TNT manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of azo dye intermediates; use in organic synthesis in preparation of toluidines, dyes, and explosives	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 dinitrotoluene or liquids containing dinitrotoluene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. If molten dinitrotoluene gets into the eyes, flush the eyes immediately with large amounts of water to remove heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If dinitrotoluene or liquids containing dinitrotoluene get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If dinitroto-

luene or liquids containing dinitrotoluene penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately. If molten dinitrotoluene gets on the skin, immediately flush the skin with water to remove heat. Wash the skin with soap or mild detergent and water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of dinitrotoluene, 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 dinitrotoluene 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 dinitrotoluene is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. For small quantities, sweep onto paper or other suitable material and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities may be reclaimed; however, if this is not practical, dissolve in fuel oil and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
4. If in the molten form, allow to cool and solidify and treat as in (3) above.

• Waste disposal methods:

Dinitrotoluene may be disposed of:

1. By making packages of dinitrotoluene in paper or other flammable material and burning in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device.
2. By dissolving dinitrotoluene in fuel oil and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR DINITROTOLUENE

Condition	Minimum Respiratory Protection* Required Above 1.5 mg/m³
Particulate or Vapor Concentration	
15 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
75 mg/m³ or less	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 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.
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.

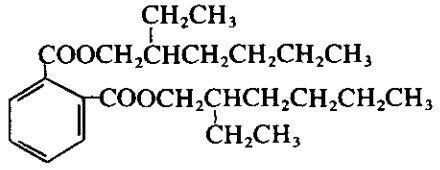
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DI-2-ETHYLHEXYL PHTHALATE (DEHP) POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about di-2-ethylhexyl phthalate (DEHP) 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:** $C_{24}H_{38}O_4$
- **Structure:**



- **Synonyms:** DEHP; 1,2-benzenedicarboxylic acid; bis(2-ethylhexyl) ester; bis(2-ethylhexyl) phthalate; DEHP; phthalic acid; bis(2-ethylhexyl) ester; di-sec octyl phthalate
- **Identifiers:** CAS 117-81-7; RTECS TI0350000; DOT not assigned
- **Appearance and odor:** Clear to slightly colored, oily, odorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 390.54
2. Boiling point (at 760 mmHg): 386°C (727°F)
3. Specific gravity (water = 1): 0.9861
4. Vapor density (air = 1 at boiling point of DEHP): 16
5. Melting point: -50°C (-58°F)
6. Vapor pressure: At 20°C (68°F), 0.01 mmHg; at 200°C (392°F), 1.32 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.005
8. Evaporation rate (butyl acetate = 1): Almost zero

- **Reactivity**

1. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, or strong acids may cause fire and explosion.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving DEHP.

- **Flammability**

1. Flash point: 218°C (425°F) (open cup)
2. Autoignition temperature: 390°C (735°F)
3. Flammable limits in air, % by volume: Lower, 0.3 at 245°C (474°F); Upper, Not available
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IIIB Combustible Liquid (29 CFR 1910.106), Flammability Rating 1 (NFPA)

- **Warning properties**

1. 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 DEHP is 5 milligrams of DEHP 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) recommends that DEHP be controlled and handled as a potential human carcinogen in the workplace, and the recommended exposure limit (REL) is that exposure be reduced to the lowest feasible limit. The use of DEHP in the quantitative fit testing of respirators should be discontinued and replaced with less toxic material such as refined corn oil. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 5 mg/m³ as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 10 mg/m³ (Table 1).

Table 1.—Occupational exposure limits for di-2-ethylhexyl phthalate

	Exposure limits mg/m³
OSHA PEL TWA	5
NIOSH REL (Ca)*	Lowest feasible limit
ACGIH TLV® TWA	5
STEL	10

* (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**

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

• **Summary of toxicology**

Effects on animals: Subchronic inhalation of DEHP by rats or mice caused pulmonary irritation, swelling, and congestion of the liver and kidneys, renal cysts, bladder stones, testicular degeneration, increased liver metabolism and liver and kidney weights, and reduced weight gain, renal concentration capacity, blood hematocrit, and cholesterol and triglyceride levels. Chronic inhalation of DEHP by mice or rats produced liver cancer. Oral administration of DEHP to mice or rats on various days during fetal development caused a reduction in implantation rates, an increase in embryolethality, delayed births, and malformations of the skeletal system and the external and central nervous systems. Two-generation reproduction studies in treated rats showed a depression in placental and fetal weights and an increase in liver and kidney weights.

• **Signs and symptoms of exposure**

Short-term (acute): Exposure to DEHP can cause gastric disturbances and diarrhea. Skin sensitization and irritation of the eyes, skin, and respiratory tract 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 DEHP, 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, gastrointestinal 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 DEHP. 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 or skin. 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 DEHP. 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 eyes, skin, liver, kidneys, gastrointestinal tract, and 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 lung function tests.

• **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 DEHP 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

• **Method**

Sampling and analysis may be performed by collecting DEHP vapors with cellulose membrane filters followed by elution with

carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure DEHP may also be used if available. A detailed sampling and analytical method for DEHP may be found in the *NIOSH Manual of Analytical Methods* (method number 5020).

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 DEHP.

SANITATION

Clothing which is contaminated with DEHP 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 DEHP from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of DEHP'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 DEHP 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 DEHP 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 DEHP 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 di-2-ethylhexyl phthalate (DEHP)

Operations	Controls
During bulk processing and application of plasticized polyvinyl chloride, polyvinylidene chloride, and other vinyl resins	Local exhaust ventilation, personal protective equipment
During hot processing of some plasticized polystyrenes, acrylics, urethanes, polyamides, and other synthetic resins	Local exhaust ventilation, personal protective equipment
During hot compounding plasticization of chlorinated rubbers and nitrile and neoprene rubbers	Local exhaust ventilation, personal protective equipment
During the application of nitrocellulose-based adhesives	Local exhaust ventilation, personal protective equipment
During hot esterification and subsequent steps in the manufacturing of DEHP	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 DEHP, an eye-wash fountain should be provided within the immediate work area for emergency use.

If DEHP 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 DEHP, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If DEHP gets on the skin, wash it immediately with soap and water. If DEHP 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 DEHP 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 DEHP, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing DEHP may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing DEHP 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 di-2-ethylhexyl phthalate (DEHP)

Condition	Minimum respiratory protection*
Any detectable concentration	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
	Any self-contained breathing apparatus with a full facepiece and 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 Dioxane*

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: $OCH_2CH_2OCH_2CH_2$
- Synonyms: Diethylene dioxide; diethylene ether; dioxan; p-dioxane; 1,4-dioxane
- Appearance and odor: Colorless liquid with a mild ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dioxane is 100 parts of dioxane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 360 milligrams of dioxane per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 1 ppm averaged over a 30-minute period, and that dioxane be regulated as an occupational carcinogen. The NIOSH Criteria Document for Dioxane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dioxane 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**

Overexposure to dioxane may cause irritation of the eyes, nose, and throat. It may also cause drowsiness, dizziness, loss of appetite, headache, nausea, vomiting, stomach pain, and liver and kidney damage. Prolonged skin exposure to the liquid may cause drying and cracking. Dioxane has been shown to induce tumor formation in experimental 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 dioxane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dioxane 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 upper respiratory system, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Dioxane may cause liver damage. A profile of liver function should be performed by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Skin disease: Dioxane 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.

—14" x 17" chest roentgenogram: Dioxane causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Dioxane 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.

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 Center for Disease Control
National Institute for Occupational Safety and Health

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

September 1978

• **Summary of toxicology**

Dioxane vapor is a mucous membrane irritant, and on prolonged exposure is toxic to the liver and kidneys. Repeated exposure of several animal species to 1000 ppm produced damage to kidneys and liver, and the repeated inhalation of 800 ppm over 30 days resulted in fatal kidney injury in some rabbits. Human volunteers exposed for 15 minutes to 300 ppm reported mild transient irritation of the eyes, nose, and throat. There is significant absorption of the liquid through the skin, adding to the inhalation hazard. Prolonged or repeated skin contact may also result in drying and cracking due to defatting action. Fatal intoxication due to liver necrosis and severe kidney damage has been reported in workers after two months of heavy exposure to dioxane vapor; the onset of poisoning was marked by drowsiness and headache, nausea, vomiting, and irritation of the eyes and respiratory passages. In one fatal case there was significant damage to the brain as well as to liver and kidney. Due to its mild odor, serious or fatal exposures have been experienced without forewarning. Tumors of the nose, liver, and lungs have been reported in animals following ingestion of high concentrations of dioxane. Immersion of chick embryoes in dioxane has been reported to cause possible mutagenic effects. The significance of these findings in humans in unknown.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 88
2. Boiling point (760 mm Hg): 101 C (214 F)
3. Specific gravity (water = 1): 1.03
4. Vapor density (air = 1 at boiling point of dioxane): 3.0
5. Melting point: 11.8 C (53 F)
6. Vapor pressure at 20 C (68 F): 29 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): 2.7

• **Reactivity**

1. Conditions contributing to instability: Heat, long exposure to moisture.
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 dioxane.
4. Special precautions: Dioxane is hydroscopic and will produce peroxides in the presence of moisture. Dioxane containing peroxides should not be distilled to dryness because of the potential explosion of nonvolatile peroxides.

• **Flammability**

1. Flash point: 12 C (54 F) (closed cup)
2. Autoignition temperature: 180 C (356 F)
3. Flammable limits in air, % by volume: Lower: 2.0; Upper: 22.0
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: Summer reports an odor threshold of 170 ppm; May reports 2.7 and 170 ppm.
2. Eye Irritation Level: Grant states that "in human beings, irritation of the eye is noted only at concentrations greater than 220 ppm of vapor in air." Patty states that at 300 ppm, dioxane "caused irritation of the eyes, nose, and throat; and at 500 ppm, it was objectionable. Even at higher concentrations, the initial irritation to eyes and respiratory passages is transitory . . . ."
3. Evaluation of Warning Properties: Patty states that the initial irritation produced by exposure to dioxane is transitory and that the "warning properties of dioxane are completely inadequate to prevent exposure to toxic amounts." The AIHA *Hygienic Guide* also notes that "the vapor has poor warning properties and can be inhaled in amounts which may cause serious intoxication or death with injury of the liver and kidneys."

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 dioxane 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 dioxane may be used. An analytical method for dioxane 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 dioxane.

• Any clothing which becomes wet with liquid dioxane should be removed immediately and non-impervious clothing which becomes contaminated with dioxane should be removed promptly and such clothing should not be reworn until the dioxane is removed from the clothing.

• Clothing wet with liquid dioxane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dioxane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dioxane, the person performing the operation should be informed of dioxane's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where liquid dioxane may contact the eyes.

SANITATION

• Skin that becomes contaminated with dioxane should be promptly washed or showered to remove any dioxane.

• Eating and smoking should not be permitted in areas where liquid dioxane is handled, processed, or stored.

• Employees who handle liquid dioxane should wash their hands thoroughly before eating, smoking, or using toilet facilities.

• Areas in which exposure to dioxane 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 dioxane may occur and control methods which may be effective in each case:

Operation	Controls
Use in spray application of natural and synthetic resin-based varnishes, lacquers, and paints	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in dipping, roller coating, tumbling, knifing, and brushing of natural and synthetic resin-based varnishes, lacquers, and paints	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for fats, oils, waxes, greases, and natural and synthetic resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a wetting agent in textile processing, dye baths, and stain and printing compositions	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a degreaser	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a dehydrating agent in preparation of histological slides	Local exhaust ventilation
Use in manufacture of detergents and cleaning preparations; manufacture of polishing compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a stabilizer for chlorinated solvents; use in preparation of cosmetics and deodorants; use in purification of drugs	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a working fluid for scintillation counter samples	General dilution ventilation; personal protective equipment
Use as a solvent in pulping of wood; polishing compounds	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 dioxane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If dioxane gets on the skin, promptly wash the contaminated skin with water. If dioxane soaks through the clothing, remove the clothing promptly and wash the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of dioxane, 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 dioxane 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 dioxane 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. Dioxane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Dioxane may be disposed of by atomizing in a suitable combustion chamber.

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 11, 1976.

RESPIRATORY PROTECTION FOR DIOXANE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
200 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 200 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 Diphenyl*

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: $C_6H_5C_6H_5$ or $C_{12}H_{10}$
- Synonyms: Biphenyl; phenylbenzene
- Appearance and odor: Colorless to pale yellow solid with a very characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diphenyl is 0.2 part of diphenyl per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1 milligram of diphenyl per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Diphenyl can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin. (It may be absorbed through the skin).

- **Effects of overexposure**

1. Short-term Exposure: Exposure to diphenyl may cause irritation of the eyes and throat.

2. Long-term Exposure: Repeated exposure to diphenyl may cause headache, nausea, indigestion, abdominal pain, fatigue, numbness, and aching of the limbs (nervous system damage), and liver damage.

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 diphenyl.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to diphenyl 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 diphenyl exposure.

—Liver disease: Exposure to high concentrations of vapor may incur damage to the liver, to which individuals with pre-existing liver disease may be more susceptible.

—Skin disease: Diphenyl can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Central nervous system disorders: Exposure to high concentrations of vapor may cause damage to the central nervous system, to which individuals with pre-existing conditions may be more susceptible.

—Kidney disease: Although diphenyl 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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

At concentrations of 5 mg/m³ or higher, irritation of the eyes and throat has been reported. Employees with repeated exposure to higher concentrations had gastrointestinal symptoms as well as polyneuritic complaints, with abnormalities of both the electroencephalogram and the electromyogram. Some showed hepatic damage detected by liver function tests and biopsy, and one fatal case of liver necrosis with some areas of cirrhosis occurred in an individual who had been exposed regularly to concentrations of vapor in air of approximately 100 mg/m³. At higher concentrations, mice and rats

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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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showed damage to the liver and kidney, as well as broncho-pulmonary effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 154
  2. Boiling point (760 mm Hg): 254 C (489 F)
  3. Specific gravity (water = 1): 1.04
  4. Vapor density (air = 1 at boiling point of diphenyl): Not applicable
  5. Melting point: 69 C (156 F)
  6. Vapor pressure at 20 C (68 F): Very low
  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: 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 diphenyl.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 113 C (235 F) (closed cup)
  2. Autoignition temperature: 538 C (1004 F)
  3. Flammable limits in air, % by volume: Lower: 0.6 at 111 C (212 F); Upper: 5.8 at 155 C (311 F)
  4. Extinguishant: Water. dry chemical, carbon dioxide, and foam.
- **Warning properties**
  1. Odor Threshold: The AIHA *Hygienic Guide* states that diphenyl has a "distinctive aromatic odor" which is detectable at 0.06 to 0.29 mg/m^3.
  2. Eye Irritation Level: Concerning eye irritation, the *Hygienic Guide* reports that "mild to moderate irritation is reported by humans exposed to the vapor." Grant reports that when concentrations of 3 to 4 ppm of Dowtherm A (a mixture of diphenyloxide (75%) and diphenyl (25%)) are reached, there is irritation of the eyes, nose, and throat."
  3. Evaluation of Warning Properties: Since the odor threshold of diphenyl is well below the permissible exposure limit, diphenyl 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 diphenyl 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 repeated or prolonged skin contact with solid diphenyl or liquids containing diphenyl.
- If employees' clothing may have become contaminated with solid diphenyl, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with diphenyl should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diphenyl from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diphenyl, the person performing the operation should be informed of diphenyl's hazardous properties.
- Non-impervious clothing which becomes contaminated with diphenyl should be removed promptly and not reworn until the diphenyl 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 molten diphenyl contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid diphenyl or liquids containing diphenyl may contact the eyes.

SANITATION

• Skin that becomes contaminated with solid diphenyl or liquids containing diphenyl should be promptly washed or showered with soap or mild detergent and water to remove any diphenyl.
• Eating and smoking should not be permitted in areas where solid diphenyl or liquids containing diphenyl are handled, processed, or stored.
• Employees who handle solid diphenyl or liquids containing diphenyl 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 diphenyl may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mixing for paper impregnation process	Local exhaust ventilation; personal protective equipment
Liberation during impregnation process for producing wrapping papers	Local exhaust ventilation
Liberation during wrapping and packaging of citrus with diphenyl-impregnated paper	Local exhaust ventilation; personal protective equipment
Liberation during use as a dye carrier for plastics and synthetic resin dyeing; during production of derivatives as diphenyl oxide	General dilution ventilation
Use as a heat-transfer medium	General dilution ventilation; personal protective equipment
Liberation during solvent applications in producing allyl alcohol from propylene oxide or phenol	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 diphenyl 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 diphenyl gets on the skin, immediately flush the contaminated skin with water. If diphenyl 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 diphenyl, 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 diphenyl 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 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 diphenyl is spilled or leaked, the following steps should be taken:
1. Remove all ignition sources.
2. Ventilate area of spill.
3. 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:
Diphenyl may be disposed of:
1. By making packages of diphenyl in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving diphenyl in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

REFERENCES

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* SPECIAL NOTE

Diphenyl appears on the Environmental Protection Agency's (EPA) Chemical Assessment Group "List of Chemicals" having substantial evidence of carcinogenicity (Environmental Protection Agency, Washington, D.C., 22 April 1980).

RESPIRATORY PROTECTION FOR DIPHENYL

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³ (0.2 ppm)
Particulate or Vapor Concentration	
10 mg/m³ (2 ppm) or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s). Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m³ (10 ppm) or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
300 mg/m³ (60 ppm) or less	A powered air-purifying chemical cartridge respirator with a full facepiece, organic vapor cartridge, 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 300 mg/m³ (60 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 Dipropylene Glycol Methyl Ether

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: $CH_3CH(OCH_3)CH_2OCH_2CH(OH)CH_3$
- Synonyms: Dipropylene glycol monomethyl ether; Dowanol 50B
- Appearance and odor: Colorless liquid with a weak odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for dipropylene glycol methyl ether is 100 parts of dipropylene glycol methyl ether per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 600 milligrams of dipropylene glycol methyl ether per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Dipropylene glycol methyl ether can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to high airborne levels or liquid splashes of dipropylene glycol methyl ether may cause irritation of the eyes and nose. Swallowing, breathing, or absorbing this chemical through the skin may cause nausea and sleepiness.

- **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 dipropylene glycol methyl ether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to dipropylene glycol methyl ether 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 dipropylene glycol methyl ether exposure.

—Liver disease: Although dipropylene glycol methyl ether 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 dipropylene glycol methyl ether 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 dipropylene glycol methyl ether 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**

Dipropylene glycol methyl ether is primarily a narcotic with mild irritating properties. Single 7-hour exposures of rats to 500-ppm vapor resulted in only mild narcosis with rapid recovery. Repeated daily inhalation exposures to four animal species at 300 to 400 ppm also produced mild narcosis but no other significant effects. These levels are disagreeable to humans, causing some eye and nasal irritation. High vapor concentrations or liquid splashes cause transient irritation of the eyes. There is no skin irritation from even prolonged or

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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repeated contact. Chronic systemic effects have not been observed in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 148
  2. Boiling point (760 mm Hg): 190 C (374 F)
  3. Specific gravity (water = 1): 0.95
  4. Vapor density (air = 1 at boiling point of dipropylene glycol methyl ether): 5.11
  5. Melting point: −83 C (−117 F)
  6. Vapor pressure at 20 C (68 F): 0.3 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): 0.02
- **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 dipropylene glycol methyl ether.
  4. Special precautions: Dipropylene glycol methyl ether will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 85 C (185 F) (closed cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Browning states that dipropylene glycol monomethyl ether has "a mild ether odor in moderate concentrations but a strong objectionable odor at 1000 ppm."
  2. Eye Irritation Level: Dipropylene glycol methyl ether vapor is not known to be an eye irritant, but, according to Patty, the undiluted liquid when placed in a rabbit's eye "on each of five consecutive days (causes) a mild transitory irritation of the conjunctival membranes."
  3. Other Information: According to Browning, "high concentrations of the vapor cause marked irritation of the nasal mucuous membrane, which is difficult for humans to tolerate."
  4. Evaluation of Warning Properties: Browning reports that nasal irritation is a warning property which "is a valuable protection against concentrations which might have toxic effects, and an inhalation hazard is not likely since, as Rowe remarks, 'levels that may be toxic on repeated exposure probably will not be tolerated voluntarily.'" The *Documentation of TLV's* notes that concentrations of 300 to 400 ppm "were very disagreeable to man; levels of 100 ppm, which might be voluntarily tolerated without complaints, were considered to be safe with respect to organic injury."

For the purposes of this guideline, dipropylene glycol methyl ether is treated as a material with good warning properties.

- **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 dipropylene glycol methyl ether 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 dipropylene glycol methyl ether may be used. An analytical method for dipropylene glycol methyl ether 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

- Clothing wet with liquid dipropylene glycol methyl ether should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of dipropylene glycol methyl ether from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the dipropylene glycol

methyl ether, the person performing the operation should be informed of dipropylene glycol methyl ether's hazardous properties.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to dipropylene glycol methyl ether may occur and control methods which may be effective in each case:

Operation	Controls
Use as a general solvent for oils and greases; use in application of coating materials	General dilution ventilation
Use as a coupling and dispersing agent in manufacture and application of printing pastes, dyes, and inks	General dilution ventilation
Use in manufacture of cosmetics	General dilution ventilation
Use in manufacture of latex paints, lacquers, and leather protective coatings	General dilution ventilation
Use as a slimicide in food packaging and adhesives in food industry	General dilution ventilation
Use as a heat-transfer agent in hydraulic brake fluid	General dilution ventilation
Use in glass cleaning, metal cleaning, and antifogging compositions	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 dipropylene glycol methyl ether 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 dipropylene glycol methyl ether saturates the clothing, promptly remove the clothing and wash or shower. Wash any dipropylene glycol methyl ether from the skin regularly. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of dipropylene glycol methyl ether, 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 dipropylene glycol methyl ether 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 dipropylene glycol methyl 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, 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 or absorbed in vermiculite, dry sand, earth, or a similar material and disposed of in a sanitary landfill.

• Waste disposal methods:

Dipropylene glycol methyl ether may be disposed of:
1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a sanitary landfill.
2. By atomizing in a suitable combustion chamber.

• American Conference of Governmental Industrial Hygienists: "Dipropylene Glycol Methyl Ether," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR DIPROPYLENE GLYCOL METHYL ETHER

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 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. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
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 and particulates. Any escape self-contained breathing apparatus.

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

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIPROPYL KETONE

INTRODUCTION

This guideline summarizes pertinent information about dipropyl ketone 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**

  $C_7H_{14}O$

- **Structure**

  $(CH_3CH_2CH_2)_2CO$

- **Synonyms**

  4-Heptanone; DPK; butyrone; GBL; Heptan-4-one; propyl ketone

- **Identifiers**

  1. CAS No.: 123-19-3
  2. RTECS No.: MJ5600000
  3. DOT UN: 2710 26
  4. DOT label: Flammable liquid

- **Appearance and odor**

  Dipropyl ketone is a combustible, colorless liquid with a pleasant but penetrating odor and a burning taste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 114.2
  2. Boiling point (760 mm Hg): 144°C (291°F)
  3. Specific gravity (water = 1): 0.82 at 15°C (59°F)
  4. Vapor density (air = 1 at boiling point of dipropyl ketone): 3.9
  5. Melting point: -32.6°C (-26.7°F)
  6. Vapor pressure at 20°C (68°F): 5.2 mm Hg
  7. Solubility: Insoluble in water; miscible with alcohol and ether.
  8. Evaporation rate: Data not available.

- **Reactivity**

  1. Conditions contributing to instability: Heat and open flame
  2. Incompatibilities: Contact of dipropyl ketone with oxidizing agents may cause a violent reaction.

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

4. Special precautions: None reported

- **Flammability**

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

1. Flash point: 49°C (120°F) (closed cup)

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-resistant foam to fight fires involving dipropyl ketone. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving dipropyl ketone 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 dipropyl ketone 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 is 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 a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dipropyl ketone. Structural firefighters' protective clothing may provide limited protection against fires involving dipropyl ketone.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dipropyl ketone [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 (235 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek for dipropyl ketone [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dipropyl ketone a threshold limit value (TLV) of 50 ppm (233 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 mild toxicity and liver effects in animals caused by exposure to high concentrations of dipropyl ketone [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Dipropyl ketone is a mild irritant of the eyes and skin and, at high concentrations, a narcotic in animals. Applied to the eyes of rabbits, dipropyl ketone produced mild irritation [NIOSH 1994]. A single application of this substance to the skin of guinea pigs caused slight irritation, but repeated applications of 0.5 ml over a 10-day period caused more serious inflammation [Clayton and Clayton 1982]. In rabbits, the dermal LD_{50} is 5,660 mg/kg [NIOSH 1994]. Fifty percent of rats inhaling a 2,690-ppm concentration of dipropyl ketone for 6 hours (LC_{50}) died; before death, these animals exhibited somnolence and respiratory depression [NIOSH 1994; Clayton and Clayton 1982]. Rats exposed to a dipropyl ketone concentration of 400 ppm for 6 hours showed signs of respiratory depression, and those exposed to 1,600 ppm for the same period became

narcotic [Clayton and Clayton 1982]. The oral LD_{50} in rats is 3,730 mg/kg [NIOSH 1994]. Rats exposed for 6 hours/day, 5 days/week for 2 weeks to a 1,200-ppm dipropyl ketone atmosphere had slightly enlarged livers, although no changes in hematology or serum chemistry were seen [Clayton and Clayton 1982]. Rats gavaged with 2,000 mg/kg dipropyl ketone for 5 days/week for 12 weeks showed signs of severe central nervous system depression and had a reduced rate of weight gain; when the dose was lowered to 1,000 mg/kg, weight gain improved and no clinical abnormalities were seen. At autopsy, however, animals in both dose groups had increased liver and kidney weights and showed hepatocyte hypertrophy [Clayton and Clayton 1982].

2. *Effects on Humans:* Contact of the skin or eyes with the liquid or vapor causes skin or eye irritation [Clayton and Clayton 1982]. Based on effects seen in animals, acute exposure to dipropyl ketone may cause central nervous system depression in humans, and chronic exposure could lead to liver damage [Clayton and Clayton 1982].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to dipropyl ketone include redness and inflammation of the eyes and eyelids, coughing and sneezing, and redness and inflammation of the skin. At higher concentrations, dizziness, sleepiness, slowed breathing, and unconsciousness may occur.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to dipropyl ketone may include enlargement of the liver, with jaundice and elevated liver enzymes, and kidney damage, with elevated urinary protein or creatinine levels and blood or pus in the urine. Dryness and cracking of the skin may occur on prolonged or repeated contact.

- **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 dipropyl ketone. ***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 dipropyl ketone 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 dipropyl ketone and lead to worker exposures to this substance:

—Use as a solvent for nitrocellulose, raw and blown oils, resins, and polymers

—Use in food flavorings and in lacquer formulations

The following methods are effective in controlling worker exposures to dipropyl ketone, 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 dipropyl ketone, 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, mucous membranes, 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 dipropyl ketone 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, mucous membranes, 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 dipropyl ketone exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dipropyl ketone on the eyes, mucous membranes, 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 dipropyl ketone.

- **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 dipropyl ketone is made using a Carbosieve S-III tube (130/65 mg sections; 60/80 mesh). 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 a carbon disulfide/dimethylformamide mixture (99:1) to extract the dipropyl ketone. 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 dipropyl ketone contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with dipropyl ketone 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 dipropyl ketone, particularly its potential to cause skin irritation.

A worker who handles dipropyl ketone 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 dipropyl ketone or a solution containing dipropyl ketone is handled, processed, or stored.

STORAGE

Dipropyl ketone 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 dipropyl ketone should be protected from physical damage and should be stored separately from oxidizing agents, reducing agents, bases, heat, sparks, and open flame. Only nonsparking tools may be used to handle dipropyl ketone. Because containers that formerly contained dipropyl ketone may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dipropyl ketone, 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, but the spray may not prevent ignition in closed spaces.
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 dipropyl ketone 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**

Dipropyl ketone 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 dipropyl ketone; 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 dipropyl ketone 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 dipropyl ketone 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 dipropyl ketone 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 dipropyl ketone. 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 dipropyl ketone 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 dipropyl ketone.

If dipropyl ketone 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 dipropyl ketone 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 dipropyl ketone. Contact lenses should not be worn if the potential exists for dipropyl ketone exposure.

REFERENCES CITED

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Clayton G, Clayton F [1982]. Patty's industrial hygiene and toxicology. 3rd rev. ed. New York, NY: John Wiley & Sons.

CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

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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.

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NIOSH [1994]. Registry of toxic effects of chemical substances databases: dipropyl ketone. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DISULFIRAM

INTRODUCTION

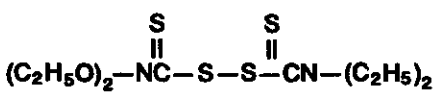
This guideline summarizes pertinent information about disulfiram for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations 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**

$C_{10}H_{20}N_2S_4$

- **Structure**



- **Synonyms**

Antabuse; bis(diethylthiocarbamoyl)disulfide; Abstensil; Alcophobin; Antethyl; Aversan; bis((diethylamino)thioxomethyl)disulphide; Disulfan; ethyl thiurad; Thiosan; tetraethylthiram disulfide; tetraethylthiuram disulfide; TTD

- **Identifiers**

1. CAS No.: 97-77-8
2. RTECS No.: JO1225000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Disulfiram is a yellow-white crystalline solid or gray powder that has a slight odor and a slightly bitter taste.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 296.54
2. Boiling point (17 mm Hg): 117°C (242.6°F)
3. Specific gravity (water = 1): 1.3 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 70°C (158°F)
6. Vapor pressure: Data not available
7. Solubility: Insoluble in water; soluble in acetone, benzene, chloroform, carbon disulfide, ether, and alcohol; slightly soluble in light petroleum.
8. Evaporation rate: Data not available

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: None reported
3. Hazardous decomposition products: Toxic gases (such

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as carbon dioxide, nitrogen dioxide, and sulfur dioxide) may be released in a fire involving disulfiram.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to disulfiram.

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 disulfiram 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 disulfiram should be moved from the fire area if it is possible to do so safely. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving disulfiram.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for disulfiram [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 disulfiram 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 limit is based on the risk of cytochrome P450 inhibition, d-amino acid inhibition, and aldehyde dehydrogenase inhibition associated with disulfiram exposure [NIOSH 1992]. The ACGIH limit is based on the risk of vasodilation, tachycardia, nausea, and hypotension associated with concomitant exposure to disulfiram and alcohol [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to disulfiram produces irritation and central nervous system effects in experimental animals. The oral LD_{50} is 500 mg/kg in rats, 1,980 mg/kg in mice, and 2,050 mg/kg in rabbits [NIOSH 1993]. The major signs of acute toxicity are ataxia, hypothermia, and paralysis [IARC 1976]. A disulfiram solution with a pH of 5.1 caused reversible and slight irritation and corneal opacity when instilled into rabbit eyes [NLM 1993]. In chronic exposure studies, rats fed disulfiram at doses of 1,000 to 2,000 mg/kg/day showed growth retardation, decreased reproductive capacity, and decreased life span [IARC 1976]. In rats exposed to disulfiram at a dose of 100 mg/kg/day from day 3 of gestation, increased fetal resorptions were seen but no teratogenic effects were observed in the surviving offspring [NLM 1993].

2. *Effects on Humans:* The human toxicology of disulfiram may be divided into those effects related to disulfiram alone and those effects associated with the combination of disulfiram and alcohol. Disulfiram alone may produce toxic effects on the nervous system, thyroid, and skin. The combination of disulfiram and alcohol causes a toxic syndrome related to elevated acetaldehyde levels (called the "Antabuse reaction"). The lowest oral dose of disulfiram reported to be lethal in an adult male is 160 mg/kg [NIOSH 1993]. Studies have shown that a small dose of disulfiram can cause a measurable effect on thyroid iodine uptake and also can cause thyroid gland hypertrophy

[Hayes 1982]. Disulfiram can also produce acneform skin rashes, dermatitis, and urticaria [Gilman et al. 1985]. Exposure to disulfiram and concomitant ingestion of alcohol produces a syndrome that begins with a sensation of heat, facial flushing, restlessness, and anxiety and progresses to palpitations, increased heart and respiratory rates, hypotension, chest pain, sweating, nausea, vomiting, weakness, dizziness, and confusion. Atypical and severe reactions have included convulsions, cardiac arrhythmias, myocardial infarction, marked respiratory depression, and acute congestive heart failure [Gosselin et al. 1984]. This syndrome has occurred in workers who have ingested alcohol and then been exposed to disulfiram, as well as to patients exposed to disulfiram as a medication [ACGIH 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to disulfiram may cause headaches, drowsiness, fatigue, dizziness, impaired sexual functioning, a garlic or metallic taste in the mouth, mild gastrointestinal symptoms, depression, psychosis, and confusion. The signs and symptoms of disulfiram-induced peripheral neuropathy may include visual impairment, muscle weakness, numbness, and tingling, and skin reactions to disulfiram exposure may include acneform eruptions, redness, swelling, scaling, and itching.

2. *Chronic exposure:* Chronic exposure to disulfiram may cause identical signs and symptoms to those associated with acute 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 disulfiram 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 disulfiram and lead to worker exposures to this substance:

—Use as a rubber accelerator and vulcanizer

—Use as a medication in the treatment of alcoholism

—Use as a seed disinfectant and fungicide

The following methods are effective in controlling worker exposures to disulfiram, 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 disulfiram, 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 a history of skin allergies and excessive alcohol intake and on the function and integrity of the central and peripheral nervous systems, eyes, skin, liver, 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 disulfiram 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 excessive alcohol intake or with diseases of the eyes, skin, nervous system, liver, 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 disulfiram exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of disulfiram on the eyes, skin, nervous system, liver, 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. Disulfiram and its metabolites can be detected in the blood, urine, and breath of exposed individuals. However, no method of correlating airborne concentrations of disulfiram with concentrations in the blood, urine, or breath has been developed. Therefore, no biological monitoring test acceptable for routine use has yet been developed for disulfiram.

- **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 disulfiram is made 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. Samples are extracted with methanol, and analysis is conducted by high-performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

If disulfiram 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 disulfiram should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles disulfiram 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 disulfiram or a solution containing disulfiram is handled, processed, or stored.

STORAGE

Disulfiram 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 disulfiram should be protected from physical damage and should be stored separately from phenols, flammable substances, heat, sparks, and open flame. Because containers that formerly contained disulfiram may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving disulfiram, 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. Remove all sources of heat and ignition.
3. Ventilate the area of the spill or leak.
4. Collect powdered material in the most convenient manner and deposit in sealed containers.

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**

  Disulfiram 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 disulfiram; 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 disulfiram 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 disulfiram 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 disulfiram 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 disulfiram. 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 disulfiram 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 disulfiram.

If disulfiram 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 disulfiram 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 disulfiram. Contact lenses should not be worn if the potential exists for disulfiram exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DIURON

INTRODUCTION

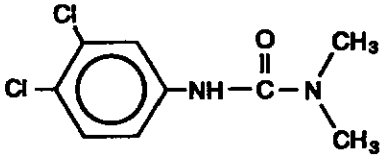
This guideline summarizes pertinent information about diuron for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may 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**

$C_9H_{10}Cl_2N_2O$

- **Structure**



- **Synonyms**

3-(3,4-Dichlorophenyl)-1,1-dimethylurea; dichlorfenidim; Crisuron; Diurex; Karmex Diuron Herbicide; Telvar Diuron Weed Killer

- **Identifiers**

1. CAS No.: 330-54-1
2. RTECS No.: YS8925000
3. DOT UN: 2767 55
4. DOT label: None

- **Appearance and odor**

Diuron is a white, odorless, crystalline solid. It is available commercially as an 80 percent wettable powder or a 35 percent aqueous suspension.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 233.1
2. Boiling point (760 mm Hg): 189° to 190°C (372.2° to 374°F) (decomposes)
3. Specific gravity: Data not available
4. Vapor density: Data not available
5. Melting point: 158° to 159°C (316.4° to 318.2°F)
6. Vapor pressure at 50°C (122°F): 0.0000031 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 and hydrocarbons; soluble in acetone.

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 (such as chlorine and oxides of nitrogen) may be released in a fire involving diuron.

4. Special precautions: Diuron hydrolyzes in fairly strong acids.

Flammability

The National Fire Protection Association has not assigned a fire hazard rating for diuron; 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 dry chemical, CO_2, water spray, fog, or standard foam to fight fires involving diuron.

Fires involving diuron 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 diuron 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 diuron. Chemical protective clothing that is specifically recommended for diuron may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving diuron.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for diuron [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 as a TWA for up to a 10-hr workday and a 40-hr workweek for diuron [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned diuron 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 1991].

- **Rationale for limits**

The NIOSH limit is based on the risk of respiratory irritation associated with diuron exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Acute exposure to diuron causes mild skin irritation and narcosis in animals, and chronic exposure to this substance may cause blood changes and spleen and liver enlargement. In contact with the unbroken skin of guinea pigs, diuron caused no irritation; in contact with broken skin, however, this substance caused a moderate degree of irritation [EPA 1987]. The dermal LD_{50} in rabbits is greater than 2,500 mg/kg [EPA 1987]. Instilled into the eyes of rabbits, diuron caused no irritation [EPA 1987]. The oral LD_{50} in rats is 1,017 mg/kg [NIOSH 1993]. Acutely poisoned animals showed signs of central

nervous system depression before death [EPA 1987]. Rats fed daily doses of diuron ranging from 2,000 to 8,000 ppm in the diet for 42 days showed decreased red blood cell counts and hemoglobin values (2,000 ppm or greater), growth retardation (4,000 ppm or greater), and increased mortality (8,000 ppm) [EPA 1987]. Rats fed diuron at a dietary dose of 5,000 ppm for 90 days showed reduced body weights, enlarged spleens, splenic hemosiderosis, and chronic methemoglobinemia [EPA 1987]. Rats fed diuron at a dietary dose of 250 ppm or higher for 2 years showed growth retardation, decreased red blood cell counts, decreased hemoglobin values, splenic hemosiderosis, and increased mortality [EPA 1987]. Oral exposure to 250 mg/kg/day of an 80 percent diuron solution on days 6 through 15 of gestation caused a statistically significant increase in wavy rib abnormalities in the offspring of rats [EPA 1987].

2. *Effects on Humans:* No information on the toxic effects of occupational exposure to diuron is available. Based on effects seen in animals, acute exposure to diuron would be expected to cause mild skin irritation and headaches, drowsiness, and incoordination in humans.

- **Signs and symptoms of exposure**

1. *Acute exposure:* No signs or symptoms of acute exposure to diuron have been reported in humans.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to diuron have been reported in humans.

- **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 diuron 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 diuron and lead to worker exposures to this substance:

—Manufacture, formulation, and use as a pre-emergence herbicide

—Use as a general weed killer and as a soil sterilant

—Use as a sugar cane flowering suppressant

The following methods are effective in controlling worker exposures to diuron, 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 diuron, 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 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 diuron 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 adverse effects on the 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 diuron exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of diuron on the 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 diuron.

- **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 diuron is made 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 60 liters is collected. Analysis is conducted by high performance liquid chromatography using ultraviolet detection. This method is described in the OSHA Computerized Information System [OSHA 1992] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

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

Clothing contaminated with diuron should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

A worker who handles diuron 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 diuron or a solution containing diuron is handled, processed, or stored.

STORAGE

Diuron 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 diuron should be protected from physical damage and should be stored separately from heat, sparks, and open flame. Because containers that formerly contained diuron may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving diuron, 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 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 diuron 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

Diuron 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 diuron is 100 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, employees 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 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 diuron 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 diuron 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 diuron 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 informa-

tion 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, and coveralls, as appropriate) should be worn to prevent skin contact with diuron. 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 diuron 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 diuron.

If diuron 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 diuron 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 diuron. Contact lenses should not be worn if the potential exists for diuron exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ENDOSULFAN

INTRODUCTION

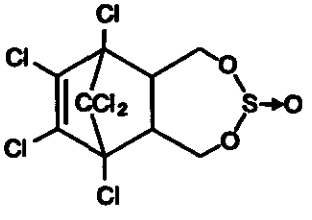
This guideline summarizes pertinent information about endosulfan for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations 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**

$C_9H_6Cl_6O_3S$

- **Structure**



- **Synonyms**

6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide; Benzoepin; Beosit; Chlorthiepin; Crisulfan; Cyclodan; Devisulphan; Endocel; Endosol; Ensure; Hildan; Insectophene; Kop-Thiodan; Malix; Niagara 5,462; Thiodan; Thifor; Thiosulfan; Tiovel

- **Identifiers**

1. CAS No.: 115-29-7
2. RTECS No.: RB9275000
3. DOT NA: 2761 55
4. DOT label: Poison

- **Appearance and odor**

Endosulfan is a tan, semi-waxy solid that is a mixture of two isomers; it may have a slight, sulfur dioxide-like odor. This substance is an organochlorine pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 406.95
2. Boiling point: 106°C (222.8°F) at 0.7 mm Hg
3. Specific gravity (water = 1): 1.75 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 108° to 110°C (226.4° to 230°F) alpha isomer; 208° to 210°C (406.4° to 410°F) beta isomer; 70° to 100°C (158° to 212°F) mixture
6. Vapor pressure at 25°C (77°F): 0.00001 mm Hg
7. Solubility: Insoluble in water; moderately soluble in most organic solvents; soluble in xylene, kerosene, chloroform, acetone, and alcohol.

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8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Heat, sparks, open flame, moisture, and air.

2. Incompatibilities: Edosulfan is incompatible with acids and alkalies (which can cause it to hydrolyze) and is corrosive to iron.

3. Hazardous decomposition products: Toxic gases (such as chlorine and oxides of sulfur) may be released in a fire involving endosulfan.

4. Special precautions: None reported

Flammability

The National Fire Protection Association had not assigned a fire hazard rating for endosulfan; this substance may burn, but it does 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, water spray, standard foam, or fog to fight fires involving endosulfan. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving endosulfan 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 endosulfan 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 endosulfan. Chemical protective clothing that is specifically recommended for endosulfan may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving endosulfan.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for endosulfan [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 for endosulfan. 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 endosulfan 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. The ACGIH also assigns a "Skin" notation to endosulfan [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of convulsions associated with endosulfan exposure and the high toxicity in experimental female animals caused by endulsofan exposure [NIOSH 1992].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Endosulfan causes central nervous system, kidney, liver, and testicular effects in animals. The dermal LD_{50} in rabbits is 90 mg/kg [NIOSH 1993]. The 4-hr LC_{50} is 80 mg/m^3 in rats [NIOSH 1993]. The oral LD_{50} is 18 mg/kg in rats and 7.4 mg/kg in mice [NIOSH 1993]. Farm animals ingesting endosulfan (dose not specified) exhibited ataxia and seizures [Hayes 1982]. Some rats given

oral doses (10 mg/kg/day) died after 15 days; at 5 mg/kg/day, rats survived but showed signs of liver damage at autopsy [Hayes 1982]. In one oral feeding study, rats tolerated endosulfan doses of 2.5 mg/kg/day for 24 months without effects, but feeding at a dose of 5 mg/kg/day for the same period reduced the growth and survival rates in female rats, caused changes in the kidneys of male rats, and caused blood changes in rats of both sexes [ACGIH 1991]. Oral doses of 10 mg/kg/day for 15 days caused degeneration of the somniferous tubules and a significant decrease in testis weight among male rats [ACGIH 1991]. A dose of 5 mg/kg/day or higher on gestation days 6 through 14 increased the mortality of rat dams and increased the rates of resorption and skeletal abnormalities in their offspring [ACGIH 1991].

2. *Effects on Humans:* Endosulfan causes central nervous system and respiratory effects in humans. The estimated lethal dose of endosulfan in humans is 50 to 500 mg/kg [Gosselin et al. 1984]. Suicides and accidental deaths have been described after acute exposure to endosulfan; these episodes resulted in gagging, vomiting, diarrhea, agitation, convulsions, foaming at the mouth, difficulty breathing, apnea, cyanosis, and loss of consciousness [Hayes 1982]. One or more seizures occurred in nine workers exposed to endosulfan while performing various tasks, including the bagging of a 50 percent water-wettable endosulfan powder. These workers experienced a prodromal syndrome consisting of malaise, nausea, vomiting, dizziness, weakness, confusion, and headache. Recovery occurred within a few days [ACGIH 1991; Hayes 1982]. In a case involving subchronic exposure, a worker cleaning vats that contained endosulfan residues developed malaise, fainting spells, and seizures; after 4 months of exposure, this worker had three consecutive seizures that resolved after emergency medical treatment. Later, gross cognitive deficits and agitation were diagnosed; 2 years later, this worker continued to have memory impairment, nominal aphasia, and poor visual-motor coordination [Aleksandrowicz 1979].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute oral exposure to endosulfan include malaise, nausea, vomiting, dizziness, weakness, confusion, headache, nervousness, agitation, tremor, seizures, convulsions, diarrhea, difficult breathing, cyanosis, and loss of consciousness. Inhalation exposure may cause nausea, confusion, excitement, flushing, and dry mouth.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to endosulfan include malaise, fainting, seizures, convulsions, agitation, cognitive impairments, and respiratory impairment (including shortness of breath and cough).

- **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:* Endosulfan 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 endosulfan 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 endosulfan and lead to worker exposures to this substance:

—Use as an insecticide for deciduous fruits, nuts, cotton and vegetables, ornamentals, tea, and coffee

—Use as an acaricide against aphids, thrips, beetles, foliar feeding larvae, cutworms, leafhoppers, the tsetse fly, and slugs

The following methods are effective in controlling worker exposures to endosulfan, 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 endosulfan, 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 assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to endosulfan 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.

- **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 endosulfan exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of endosulfan 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 endosulfan.

- **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 endosulfan is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) and an enclosed glass fiber filter. Samples are collected at a recommended flow rate of 1.0 liter/min until a recommended air volume of 60 liters is collected. Analysis is conducted by gas chromatography using an electron capture detector. This method is described in the OSHA Computerized Information System [OSHA 1993].

PERSONAL HYGIENE

Endosulfan can be absorbed through the skin in toxic amounts. Therefore, if endosulfan 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 endosulfan 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 endosulfan, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles endosulfan 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 endosulfan or a solution containing endosulfan is handled, processed, or stored.

STORAGE

Endosulfan 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 endosulfan should be protected from physical damage and should be stored separately from alkalies, acids, heat, sparks, and open flame. Because containers that formerly contained endosulfan may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving endosulfan, 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 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, take up with sand or other noncombustible absorbent material and place into of the spill to contain the endosulfan 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**

  The owners and operators of a facility must comply with EPA's emergency planning requirements if 1 lb or more of endosulfan 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 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 endosulfan 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 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 endosulfan 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. Endosulfan 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. P050. Endosulfan is approved for land disposal as long as the concentration of endosulfan in the waste or treatment residual does not exceed 0.13 mg/kg. Endosulfan 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, rele-

vant 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 endosulfan 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 endosulfan. 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. One source recommends the use of protective gloves and clothing made of Viton or neoprene for protection against permeation by endosulfan.

If endosulfan 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 endosulfan 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 endosulfan. Contact lenses should not be worn if the potential exists for endosulfan exposure.

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Occupational Health Guideline for Endrin

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: $C_{12}H_8Cl_6O$
- Synonyms: 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonaphthalene
- *Appearance and odor: Colorless to tan solid with a* mild chemical odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for endrin is 0.1 milligram of endrin per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Endrin 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 endrin may cause sudden convulsions which may occur from 30 minutes to 10 hours after exposure. Headache, dizziness, sleepiness, weakness, and loss of appetite may be present for two to four weeks following this exposure. A number of deaths have occurred from swallowing endrin. In less severe cases of endrin poisoning, the complaints include headache, dizziness, abdominal discomfort, nausea, vomiting, insomnia, agitation, and mental confusion. Experimental feeding of endrin to animals has produced abnormalities in their offspring.

- **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 endrin.

- ***Recommended medical surveillance***

The following medical procedures should be made available to each employee who is exposed to endrin 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 and liver should be stressed. The concentration of endrin in the blood is helpful in determining the extent of absorption.

2. Periodic Medical Examination: The aforementioned medical examination should be repeated on an annual basis.

- **Summary of toxicology**

Endrin as the dust or in solution is a convulsant. Single doses of 2.5 mg/kg of endrin administered orally to pregnant golden hamsters during the period of fetal organogenesis caused a high incidence of fetal deaths, congenital anomalies, and growth retardation. Rats fed a diet of 50 or 100 ppm endrin for 2 years developed degenerative changes in the liver. In humans, the first effect of endrin intoxication is frequently a sudden epileptiform convulsion, which may occur from 30 minutes to up to 10 hours after overexposure; it lasts for several minutes and is usually followed by a stuporous state for 15 minutes to 1 hour. The electroencephalogram may show dysrhythmic changes which frequently precede convulsions; withdrawal from exposure usually results in a normal electroencephalogram within 1 to 6 months. In most cases recovery is rapid, but headache, dizziness, lethargy, weakness, and anorexia may persist

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 2 to 4 weeks. In less severe cases of endrin intoxication, the complaints are headache, dizziness, abdominal discomfort, nausea, vomiting, insomnia, agitation and, occasionally, slight mental confusion. There are numerous reports of fatalities from ingestion of endrin. In one nonfatal incident, ingestion of bread made with endrin-contaminated flour resulted in sudden convulsions in three people; in one person the serum endrin level was 0.053 ppm 30 minutes after the convulsion and 0.038 ppm after 20 hours; in the other two cases no endrin was detected in the blood at 8.5 or 19 hours, respectively, after convulsions.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 380.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of endrin): Not applicable
5. Melting point: 200 C (392 F) decomposes
6. Vapor pressure at 20 C (68 F): 0.0000002 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 160 ppb
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 200 C (392 F) cause a chemical change that gives off heat and may cause containers to burst. If a solvent is present, flammable vapors may be formed from it.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids may cause evolution of heat and formation of explosive solvent vapors.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, other volatile chlorinated compounds, and carbon monoxide) may be released when endrin decomposes.
4. Special precautions: None

- **Flammability**

1. Solid not combustible; may be dissolved in flammable solvent

- **Warning properties**

Since the vapor pressure of endrin is negligible, warning properties are not considered.
Endrin 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 endrin 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 endrin or liquids containing endrin.
- If employees' clothing has had any possibility of being contaminated with endrin or liquids containing endrin, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with endrin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of endrin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the endrin, the person performing the operation should be informed of endrin's hazardous properties.
- Where there is any possibility of exposure of an employee's body to endrin or liquids containing endrin, 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 endrin should be removed immediately and not reworn until the endrin 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 endrin or liquids containing endrin contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to endrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with endrin should be immediately washed or showered with soap or mild detergent and water to remove any endrin.

• Workers subject to skin contact with endrin or liquids containing endrin should wash with soap or mild detergent and water any areas of the body which may have contacted endrin at the end of each work day.

• Eating and smoking should not be permitted in areas where endrin or liquids containing endrin are handled, processed, or stored.

• Employees who handle endrin or liquids containing endrin 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 endrin may occur and control methods which may be effective in each case:

Operation	Controls
Application as an insecticide on cotton fields and vegetable crops, and as a rodenticide against mice and chipmunks in orchards	Personal protective equipment
Formulation for use as an insecticide and rodenticide	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of endrin	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 endrin or liquids containing endrin 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 endrin or liquids containing endrin get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If endrin or liquids containing endrin penetrate 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 endrin, 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 endrin or liquids containing endrin 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 endrin 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 endrin should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Endrin may be disposed of in sealed containers in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on endrin, look up endrin 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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RESPIRATORY PROTECTION FOR ENDRIN

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
1 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.
5 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 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.
100 mg/m³ or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. 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.
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 endrin; 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 Epichlorohydrin*

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_5OCl
- Synonyms: 1-Chloro-2,3-epoxypropane; 2-chloropropylene oxide; gamma-chloropropylene oxide
- Appearance and odor: Colorless liquid with an irritating chloroform-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for epichlorohydrin is 5 parts of epichlorohydrin per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 19 milligrams of epichlorohydrin per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 2 mg/m³ (0.5 ppm) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 19 mg/m³ averaged over a 15-minute period. The NIOSH Criteria Document for Epichlorohydrin should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Epichlorohydrin 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.

- **Effects of overexposure**

1. Short-term Exposure: Epichlorohydrin may cause irritation of the eyes, respiratory tract, and skin. Nausea and vomiting may also occur. Coughing, difficult breathing, and a blue coloration of the skin may be present. Liquid epichlorohydrin may produce blistering and deep-seated pain on contact with the skin. The liquid is highly irritating to the eyes. Breathing difficulty may occur several hours after exposure. A person may become sensitized to this chemical so that even very small amounts cannot be tolerated.

2. Long-term Exposure: Repeated or prolonged skin contact with epichlorohydrin may cause skin burns. Repeated or prolonged contact with this chemical might also cause liver, lung, and kidney injury. Antifertility effects, including persistent sterility, have been induced in animals exposed to epichlorohydrin.

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 epichlorohydrin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to epichlorohydrin 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 eyes, hematopoetic and respiratory systems, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Epichlorohydrin may cause human lung damage. Surveillance of the lungs is indicated.

—Pulmonary function testing of FVC and FEV (1 sec): Epichlorohydrin is a severe pulmonary irritant in animals.

—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.

—Eye disease: Epichlorohydrin is a severe eye irritant and may cause tissue damage. Those with pre-

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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.

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

existing eye problems may be at increased risk from exposure.

—Liver function tests: Epichlorohydrin may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Epichlorohydrin is a defatting agent and can cause dermatitis on prolonged exposure. It can also cause burning, itching, blisters, skin erosion, redness, and residual erythema which may occur from a few minutes to several hours after exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Medical warning: Employees should be informed that large doses of epichlorohydrin have caused antifertility effects in animals; however, no effects have been found on potency.

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**

Epichlorohydrin vapor is a potent eye and respiratory irritant. The LC50 for rats was 500 ppm for 4 hours; the animals showed gradual development of cyanosis followed by muscular relaxation of the extremities, but not narcosis. Rats exposed repeatedly to 120 ppm for 6-hour periods showed lung, liver, and kidney injury; some respiratory distress was observed at 56 ppm, while 9 ppm produced no effects. The liquid is markedly irritating when instilled in the eye and intensely irritating to the depilated skin of laboratory animals, leading to widespread necrosis. Subcutaneous injection of epichlorohydrin in animals has been reported to cause sarcoma at the site of injection. In man, contact of the liquid with the skin at first produces a slight transient burning sensation which may be followed several hours later by blistering and pain in the region of contact; it is also highly irritating to the eyes. An occasional case of sensitization with resulting intolerance to very small quantities of the substance has been reported. At 25 ppm the odor is recognized by the majority of persons; one report indicated eye and nose irritation only at levels exceeding 100 ppm while another stated that 40 ppm at the site of a spill caused immediate eye, nose, and throat irritation. The earliest symptoms of intoxication may be referable to the gastrointestinal tract (nausea, vomiting, abdominal discomfort) or pain in the region of the liver; labored breathing, cough, and cyanosis may be evident; the onset of chemical pneumonitis may occur several hours after exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 92.5
2. Boiling point (760 mm Hg): 115 C (239 F)
3. Specific gravity (water = 1): 1.18
4. Vapor density (air = 1 at boiling point of epichlorohydrin): 3.19
5. Melting point: −58 C (−72 F)
6. Vapor pressure at 20 C (68 F): 13 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 6.4
8. Evaporation rate (butyl acetate = 1): 1.35

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 325 C (617 F) will cause epichlorohydrin to polymerize.
2. Incompatibilities: Contact with strong acids, caustics, zinc, aluminum, chlorides of iron and aluminum and strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, hydrogen chloride, and carbon monoxide) may be released in a fire involving epichlorohydrin.
4. Special precautions: Epichlorohydrin will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 37.8 C (100 F) (closed cup)
2. Autoignition temperature: 415.6 C (780 F)
3. Flammable limits in air, % by volume: Lower: 3.8; Upper: 21.0
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

The AIHA *Hygienic Guide* states that 5 ppm of epichlorohydrin, the permissible exposure limit, cannot be detected by odor. At 16 ppm, four humans "detected the presence of epichlorohydrin, but only two could identify it;" at 64 ppm, all four could recognize the odor. In another investigation, half of a group of people detected 10-12 ppm, and within 5 minutes all of the subjects detected 25 ppm. According to the *Hygienic Guide*, "the threshold for nose and eye irritation is reported to be greater than 100 ppm." Since the warning properties of epichlorohydrin do not become evident until concentrations are several times the permissible exposure limit, epichlorohydrin is treated as a material with poor warning properties.

Epichlorohydrin is an eye irritant. The NIOSH Criteria Document cites data indicating that exposure to 20 ppm for one hour causes temporary burning of the eye and nasal passages.

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 epichlorohydrin. 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 epichlorohydrin may be used. An analytical method for epichlorohydrin 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 epichlorohydrin.

• Clothing contaminated with liquid epichlorohydrin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of epichlorohydrin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the epichlorohydrin, the person performing the operation should be informed of epichlorohydrin's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid epichlorohydrin, 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 liquid epichlorohydrin should be removed immediately and not reworn until the epichlorohydrin 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 epichlorohydrin contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid epichlorohydrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid epichlorohydrin should be immediately washed or showered with soap or mild detergent and water to remove any epichlorohydrin.

• Eating and smoking should not be permitted in areas where liquid epichlorohydrin is handled, processed, or stored.

• Employees who handle liquid epichlorohydrin 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 epichlorohydrin may occur and control methods which may be effective in each case:

Operation	Controls
Use as intermediate in manufacture of DGEBA resins, epoxy novolac resins, phenoxy resins, and wet-strength resins for paper	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of glycerol and glycidol derivatives for use as as plasticizer, stabilizer solvent, intermediate, dyestuff surfactants, pharmaceuticals, and intermediates for further synthesis	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Use as stabilizer in manufacture of chlorinated rubber and chlorinated insecticides	Process enclosure; local exhaust ventilation; personal protective equipment
Use in coating fibers and textile surface coatings	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 epichlorohydrin 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 epichlorohydrin gets on the skin, immediately flush the contaminated skin using soap or mild detergent and water. If epichlorohydrin soaks through the clothing, remove the clothing immediately and flush 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 epichlorohydrin, 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 epichlorohydrin 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 epichlorohydrin 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. Epichlorohydrin 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 epichlorohydrin vapors are permitted.

• Waste disposal method:

Epichlorohydrin may be disposed of by atomizing 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 11, 1976, and Volume 18, 1978.

RESPIRATORY PROTECTION FOR EPICHLOROHYDRIN

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
250 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 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 and acid gases. 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.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of epichlorohydrin; 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 250 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for EPN

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: $(4\text{-}NO_2C_6H_4O)(C_2H_5O)C_6H_5PSo$ $C_{14}H_{14}NO_4PS$
- Synonyms: O-ethyl O-p-nitrophenyl thionobenzenephosphonate; O-ethyl O-p-nitrophenyl benzenephosphonothioate
- Appearance: Yellow solid or brown liquid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for EPN is 0.5 milligram of EPN per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

EPN 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 EPN, 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 EPN, 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, slow heartbeat, convulsions and coma may occur.

2. Long-term Exposure: Repeated exposure to EPN may make a person more susceptible to the effects of this and related chemicals. Repeated exposure 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 EPN.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to EPN 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 disorders.

—Cholinesterase determination: EPN causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity 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

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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time overexposure is suspected or signs and symptoms of toxicity occur.

• **Summary of toxicology**

EPN is an anticholinesterase agent; absorption may occur from inhalation of the dust or mist, from skin absorption of solutions, or from ingestion. 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. In animals, EPN has produced a demyelination syndrome.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 323.3
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of EPN): Not applicable
5. Melting point: 36 C (97 F)
6. Vapor pressure at 20 C (68 F): 0.0003 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 with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of sulfur and nitrogen, phosphoric acid mist, and carbon monoxide) may be released when EPN decomposes.
4. Special precautions: Liquid EPN will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of EPN.
2. Eye Irritation Level: EPN 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 EPN, it is treated as a material with poor warning properties. The Pennsylvania *Hygienic Information Guide* for EPN states that the "lack of odor and warning signs, as well as the delayed onset of symptoms, make EPN a dangerous material to work with."

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 EPN using a filter with subsequent recovery with iso-octane and gas chromatrographic analysis. A detailed analytical method for EPN 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 T" (order number PB 262 404).

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 EPN or liquids containing EPN.

• If employees' clothing has had any possibility of being contaminated with EPN or liquids containing EPN, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with EPN should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of EPN from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the EPN, the person performing the operation should be informed of EPN's hazardous properties.

• Where there is any possibility of exposure of an employee's body to EPN or liquids containing EPN, 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 EPN should be removed immediately and not reworn until the EPN 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 EPN or liquids containing EPN contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to EPN or liquids containing EPN, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with EPN should be immediately washed or showered with soap or mild detergent and water to remove any EPN.

• Workers subject to skin contact with EPN or liquids containing EPN should wash with soap or mild detergent and water any areas of the body which may have contacted EPN at the end of each work day.

• Eating and smoking should not be permitted in areas where EPN or liquids containing EPN are handled, processed, or stored.

• Employees who handle EPN or liquids containing EPN 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 EPN may occur and control methods which may be effective in each case:

Operation	Controls
Formulation for use as an insecticide and acaricide	Process enclosure; dust collection; personal protective equipment; general dilution ventilation
Application as an insecticide and acaricide on agricultural crops, vegetables, fruit trees, and ornamentals	Material substitution; personal protective equipment
Manufacture of EPN	Process enclosure; general dilution ventilation; personal protective equipment; 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 EPN or liquids or mists containing EPN 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 EPN or liquids or mists containing EPN get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If EPN or liquids or mists containing EPN 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 EPN, 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 EPN or liquids containing EPN 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 EPN is spilled, the following steps should be taken:
1. Ventilate area of spill.
2. Cover with soda ash, mix and spray with water. Place in a container of water and allow to stand for two days, then neutralize with 6 molar HCl.
• Waste disposal method:
EPN may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR EPN

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.
25 mg/m³ or less	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 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.
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 EPN; 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 50 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Ethanolamine

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: $HOCH_2CH_2NH_2$
- Synonyms: Ethylolamine; monoethanolamine; beta-aminoethyl alcohol; 2-aminoethanol; 2-hydroxyethylamine
- Appearance and odor: Colorless liquid with a mild ammonia-like odor. It can be a solid below 10.3 C (51 F).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethanolamine is 3 parts of ethanolamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of ethanolamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethanolamine 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: Ethanolamine may cause nose, eye, and skin irritation.

2. Long-term Exposure: Prolonged or repeated skin contact with liquid ethanolamine 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 ethanolamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethanolamine 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 ethanolamine exposure.

—Skin disease: Ethanolamine may cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Ethanolamine causes liver damage in animals and this justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Ethanolamine causes kidney damage in animals and this justifies special consideration before exposing those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethanolamine might cause exacerbation of symptoms.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethanolamine vapor is a skin, eye, and respiratory irritant, and has significant narcotic properties. In animals exposed repeatedly to 66 to 100 ppm, some animals died during 24 to 30 days of exposure, and all animals were lethargic. Dogs and cats exposed to 2.47 mg/l (990 ppm) for 4 days survived but four of six guinea pigs died from exposure to 0.58 mg/l (233 ppm) for 1 hour; pathologic changes were chiefly those of pulmonary irritation, with some non-specific changes in the liver and kidneys. No mortality or pathology resulted from 90 days of continuous exposure of dogs to 26 ppm, of rats to 12 ppm, or of guinea pigs to 15 ppm. The liquid produced moderate irritation of the skin of rabbits and

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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severe irritation in the eyes of rabbits. When applied to human skin for 1-½ hours, marked redness of the skin occurred. No systemic effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 61.1
2. Boiling point (760 mm Hg): 170 C (338 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of ethanolamine): 2.1
5. Melting point: 10.3 C (51 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): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids may cause spattering.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving ethanolamine.
4. Special precautions: Liquid ethanolamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 85 C (185 F) (closed cup)
2. Autoignition temperature: 780 C (1436 F)
3. Flammable limits in air, % by volume: Lower: 5.5 (calculated); Upper: 17 (estimated)
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Ethanolamine has a mild ammonia-like odor, which the AIHA *Hygienic Guide* reports is noticeable at 2 to 3 ppm.
2. Eye Irritation Level: The *Hygienic Guide* states that ethanolamine is an eye irritant, but do not specify whether both liquid and vapor have this effect. Grant reports that "a drop of ethanolamine applied to rabbit eyes causes injury similar to that caused by ammonia, but slightly less severe." The available literature does not specifically report that the vapor of ethanolamine produces eye irritation. By analogy with ammonia, ethanolamine is treated as an eye irritant for the purposes of this guideline.
3. Other Information: The *Hygienic Guide* reports that ethanolamine is a respiratory tract irritant. The concentrations producing this irritation are not given.
4. Evaluation of Warning Properties: Since ethanolamine has an odor threshold which is at or below the permissible exposure limit, it is treated as a substance 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 ethanolamine 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 repeated or prolonged skin contact with liquid or solid ethanolamine.
- If employees' clothing may have become contaminated with solid ethanolamine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with liquid or solid ethanolamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethanolamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethanolamine, the person performing the operation should be informed of ethanolamine's hazardous properties.

• Non-impervious clothing which becomes contaminated with liquid or solid ethanolamine should be removed promptly and not reworn until the ethanolamine 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 or solid ethanolamine contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid or solid ethanolamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid or solid ethanolamine should be promptly washed or showered to remove any ethanolamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethanolamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in production of monoalkanolamides for nonionic detergents, emulsifiers, and soaps; fuel oil additives; water-in-oil emulsifiers; pharmaceuticals; agricultural chemicals; cosmetics; emulsion paints; polishers, and cleansers	Process enclosure; local exhaust ventilation
Use during synthesis of acelethanolamine in manufacture of inks, paper, glues, textiles, and polishes; syntheses of phenylethanolamine for acetate rayon dyes, dyestuffs; synthesis of tolyethanolamine in emulsifiers and dyestuffs	Process enclosure; local exhaust ventilation
Use during synthesis of 2-mercaptothiazole in rubber vulcanization acceleration	Process enclosure; local exhaust ventilation; personal protective equipment
Use in recovery and removal of acid gases from natural, fuel, and process gas in synthesis of ammonia; use in dry ice manufacture	Process enclsoure; 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 ethanolamine 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 ethanolamine gets on the skin, promptly flush the contaminated skin with water. If ethanolamine soaks 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 ethanolamine, 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 ethanolamine 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 ethanolamine 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 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 reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

4. If in solid form, allow to melt and follow (3) above.

• Waste disposal methods:

Ethanolamine 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.

REFERENCES

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RESPIRATORY PROTECTION FOR ETHANOLAMINE

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Vapor Concentration	
30 ppm or less	A chemical cartridge respirator which provides protection against ethanolamine.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
150 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) which provides protection against ethanolamine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A gas mask with a chin-style or a front- or back-mounted canister which provides protection against ethanolamine.
1000 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 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 ethanolamine. 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 ETHION

INTRODUCTION

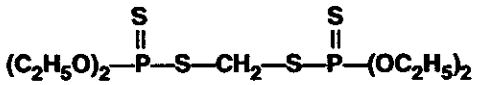
This guideline summarizes pertinent information about ethion for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may 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**

$C_9H_{22}O_4P_2S_4$

- **Structure**



- **Synonyms**

bis(S-(Diethoxyphosphinothioyl)mercapto)methane; ethyl methylene phosphorodithioate; O,O,O',O'-tetraethyl S,S'-methylene di(phosphorodithioate); phosphorodithioic acid, O,O-diethyl ester, S,S-diester with methanedithiol; Bladan; Diethion; Embathion; Ethanox; Ethodan; Fosfono 50; Hylemox; Niagra 1240; Nialate; Rhodiacide; Rhodocide; Soprathion

- **Identifiers**

1. CAS No.: 563-12-2
2. RTECS No.: TE4550000
3. DOT NA: 2783 55
4. DOT label: Poison

- **Appearance and odor**

Ethion is a colorless liquid that is odorless when pure. Ethion is marketed in several forms: as granules, a wettable powder, a dust, and in various oil solutions and combinations with other materials. Technical grade ethion has a very disagreeable odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 384.48
2. Boiling point (760 mm Hg): Decomposes above 150°C (302°F)
3. Specific gravity (water = 1): 1.22 at 20°C (68°F)
4. Vapor density: Data not available
5. Freezing/melting point: -12° to -13°C (8.6° to 10.4°F)

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6. Vapor pressure at 25°C (77°F): 0.0000015 mm Hg

7. Solubility: Slightly soluble in water; soluble in acetone, methyl alcohol, ethyl alcohol, xylene, chloroform, methylated naphthalene, and petroleum oils.

8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Ethion is incompatible with alkaline formulations.

3. Hazardous decomposition products: Toxic gases (such as oxides of sulfur and phosphorus) may be released in a fire involving ethion.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a fire hazard rating for ethion.

1. Flash point: 176°C (348.8°F)

2. Autoignition temperature: Data not available

3. Flammable limits: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, fog, or standard foam to fight fires involving ethion. 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 ethion 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 ethion 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. 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 ethion. Chemical protective clothing that is specifically recommended for ethion may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving ethion.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethion [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 0.4 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek for ethion. 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 ethion a threshold limit value (TLV) of 0.4 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 ethion [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of cholinesterase inhibition and toxic effects on the nervous, respiratory, and digestive systems associated with ethion exposure [NIOSH 1992]. The ACGIH limit is based on the risk of organophosphate poisoning associated with exposure to ethion [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Ethion is an organophosphate pesticide that produces its effects by inhibiting cholinesterase activity in the central nervous system.

Instilled into the eyes of rabbits, 0.05 ml of ethion caused immediate irritation without corneal injury [NLM 1993]. The dermal LD_{50} is 62 mg/kg in rats and 915 mg/kg in guinea pigs [NIOSH 1993]. The LC_{50} in rats is 864 mg/m3 for an unspecified period [NIOSH 1993]. The oral LD_{50} is 13 mg/kg in rats and 40 mg/kg in mice [NIOSH 1993]. Rats fed ethion at a dietary level of 300 ppm for 28 days developed marked cholinesterase inhibition, and those fed dietary levels of 600 to 1,500 ppm showed complete cholinesterase inhibition [NLM 1993].

2. *Effects on Humans:* Ethion is an organophosphate pesticide that causes cholinesterase inhibition in humans. The lethal oral dose in humans is estimated to be 50 to 500 mg/kg [Gosselin et al. 1984]. Ethion is reported to have caused organophosphate poisoning in peach and grape pickers who were applying this pesticide [ACGIH 1991]. In an in vitro culture, ethion caused a significant increase in the frequency of sister chromatid exchanges in human lymphoid cells [NLM 1993].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute oral exposure causes severe gastrointestinal effects, such as cramps, diarrhea, nausea, and anorexia. Acute inhalation causes wheezing, difficult breathing, blurred vision, constricted pupils, and tearing. Acute dermal exposure causes localized twitching and sweating. Severe overexposure by any route can cause respiratory paralysis, coma, and death.

2. *Chronic exposure:* Repeated exposure to small amounts of ethion may cause acetylcholine buildup and lead to the signs and symptoms of poisoning described above for acute exposure.

- **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 ethion from the eyes with large amounts of water for at least 15 min, occasionally lifting the lower and upper eyelids. If irritation persists, get medical attention as soon as possible.

2. *Skin exposure:* Ethion 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:* 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 esposure:* Take the following steps if ethion or a solution containing this substance 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 ethion and lead to worker exposures to this substance:

—Use as an insecticide and acaricide for citrus fruit, apples, nuts, deciduous fruit, and cotton

—Use as a cattle dip for ticks and as a treatment for buffalo flies

—Use for the control of aphids, mites, scales, thrips, leafhoppers, maggots, and foliar feeding larvae on a wide variety of food, fiber, and ornamental crops

The following methods are effective in controlling worker exposures to ethion, 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 ethion, 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 red blood cell and plasma cholinesterase activity.

  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 ethion 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 red blood cell or plasma 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 ethion exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethion on red blood cell or plasma 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 red blood cell cholinesterase (RBC ChE) is a nonspecific qualitative indicator of exposure to organophosphorus chemicals such as ethion. Inhibition of RBC ChE can be an indicator either of acute overexposure or of cumulative chronic exposure, depending on the intensity and duration of exposure. Individual pre-exposure levels of enzyme activities should be determined by measuring RBC ChE activity in blood samples collected on two occasions (at least 3 days apart) before exposure begins or following at least 30 days without exposure; the same method and laboratory should be used for sampling and analysis. An RBC ChE activity level that is equal to 70 percent of the individual's baseline is recommended by some sources as a Biological Exposure Index (BEI) for exposure to organophosphorus chemicals.

- **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 ethion is made 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 480 liters is collected. The sample is then treated with toluene to extract the ethion. Analysis is conducted by gas chromatography using a flame photometric detector. This method is described in the OSHA Computerized Information System [OSHA 1993] and the *OSHA Chemical Information Manual* [OSHA 1987].

PERSONAL HYGIENE

Ethion can be absorbed through the skin in toxic amounts. Therefore, if ethion contacts the skin, workers should wash the affected areas repeatedly and vigorously with soap and water.

Clothing contaminated with ethion 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 ethion, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles ethion 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 ethion or a solution containing ethion is handled, processed, or stored.

STORAGE

Ethion 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 ethion should be protected from physical damage and should be stored separately from food or feed products, heat, sparks, and open flame. Because containers that formerly contained ethion may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethion, 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 the area of the spill or leak.
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, 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 ethion for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous waste, 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**

The owners or operators of a facility must comply with EPA's emergency planning requirements [40 CFR 355.30] if 1,000 lb or more of ethion are present.

- **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 ethion 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 ethion 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 ethion 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 ethion

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 gloves and clothing should be worn to prevent any skin contact with ethion. 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 for use against permeation by ethion and may provide protection for periods greater than 4 but less than 8 hours. Natural rubber has a breakthrough time of less than 1 hr and is therefor not recommended for use against permeation by ethion.

If ethion 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 ethion 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 ethion.

REFERENCES CITED

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Occupational Health Guideline for 2-Ethoxyethanol

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: $C_2H_5OCH_2CH_2OH$
- Synonyms: Ethyleneglycol monoethyl ether; Cellosolve (R) solvent
- Appearance and odor: Colorless liquid with a sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2-ethoxyethanol is 200 parts of 2-ethoxyethanol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 740 milligrams of 2-ethoxyethanol 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 2-ethoxyethanol from 100 ppm to 50 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Ethoxyethanol 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**

In animal experiments 2-ethoxyethanol has caused liver, kidney, and lung damage and anemia due to the destruction of red blood cells. It has also caused 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 2-ethoxyethanol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2-ethoxyethanol 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-ethoxyethanol exposure.

—Chronic respiratory disease: 2-Ethoxyethanol causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 2-ethoxyethanol might cause exacerbation of symptoms due to its irritant properties.

—Blood disease: 2-Ethoxyethanol causes in animals an increase in red cell fragility, decreased levels of red cells and hemoglobin, and an increase in immature white cells. Persons with anemia may be at increased risk from exposure.

—Kidney disease: 2-Ethoxyethanol 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: 2-Ethoxyethanol is absorbed through the skin. Persons with chronic skin disorders characterized by eczema or fissures may be at added risk of absorption of toxic amounts.

—Liver disease: Although 2-ethoxyethanol 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.

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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• **Summary of toxicology**

2-Ethoxyethanol vapor is toxic to the lungs, kidneys, and hematopoietic system in animals. In mice the LC50 for 7 hours was 1820 ppm; death was attributed to lung and kidney injury. In rabbits, repeated daily doses of 1 ml/kg given orally caused albuminuria and hematuria on the 7th day with death on the 8th day due to kidney injury. Dogs repeatedly exposed to 840 ppm for 12 weeks developed a slight decrease in red cells and hemoglobin and an increase in immature white cells. In female rats exposed to 125 ppm for 4 hours, there was an increase in erythrocyte fragility. Of two workers employed for 3 years in factories using 2-ethoxyethanol as a solvent, one had a slight yellowish discoloration of the sclera and the other had trace albuminuria and a slightly increased level of bilirubin in the blood. The liquid instilled in the eyes of animals caused immediate discomfort, some conjunctival irritation, and a slight transitory irritation of the cornea which was readily reversible. Repeated and prolonged contact of the liquid with the skin of rabbits caused only a mild irritation, but toxic amounts were readily absorbed through the skin.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 90.1
2. Boiling point (760 mm Hg): 135 C (275 F)
3. Specific gravity (water = 1): 0.93
4. Vapor density (air = 1 at boiling point of 2-ethoxyethanol): 3.0
5. Melting point: −70 C (−94 F) (pour point)
6. Vapor pressure at 20 C (68 F): 4 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): Less than 1

• **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.
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 2-ethoxyethanol.
4. Special precautions: 2-Ethoxyethanol will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 49 C (120 F) (closed cup)
2. Autoignition temperature: 235 C (455 F)
3. Flammable limits in air, % by volume: Lower: 1.8; Upper: 14
4. Extinguishant: "Alcohol" foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that 2-ethoxyethanol has "a slight odor at low concentrations and a disagreeable odor at high concentrations." Grant states that this substance "is a practically odorless liquid."
2. Eye Irritation Level: Grant states that "exposure of rabbits to high vapor concentrations causes symptoms of ocular and respiratory irritation, but even at concentrations which are probably lethal, causes no significant ocular injury."
3. Other Information: The *Hygienic Guide* states that "high vapor concentrations can cause irritation of the nose and throat." No quantitative information is available, however, concerning the thresholds of irritation.
4. Evaluation of Warning Properties: Since eye, nose and throat irritation occur only at high levels, and since Grant points out that this substance is almost odorless, 2-ethoxyethanol 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 2-ethoxyethanol 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 2-ethoxyethanol.

• Clothing wet with 2-ethoxyethanol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-ethoxyethanol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 2-ethoxyethanol, the person performing the operation should be informed of 2-ethoxyethanol's hazardous properties.

• Non-impervious clothing which becomes contaminated with 2-ethoxyethanol should be removed promptly and not reworn until the 2-ethoxyethanol is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid 2-ethoxyethanol may contact the eyes.

SANITATION

• Skin that becomes contaminated with 2-ethoxyethanol should be promptly washed or showered to remove any 2-ethoxyethanol.

• Employees who handle liquid 2-ethoxyethanol should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2-ethoxyethanol may occur and control methods which may be effective in each case:

Operation	Controls
Use as solvent in manufacture of lacquers, lacquer thinners, nitrocellulose lacquers, alkyd resins, printing ink solvents, varnish removers, cleaning compounds, soaps, cosmetics, pesticides, pharmaceuticals, adhesives, and detergents; during use in textile dyeing and printing and manufacture of leather finishes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as anti-icing additive in manufacture of brake fluids, aviation fuels, and automotive anti-stall additives	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 2-ethoxyethanol 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 2-ethoxyethanol gets on the skin, promptly flush the contaminated skin with water. If liquid 2-ethoxyethanol soaks through the clothing, promptly flush the skin with water. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of 2-ethoxyethanol, 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-ethoxyethanol 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 2-ethoxyethanol 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. 2-Ethoxyethanol 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 2-ethoxyethanol vapors are permitted.

• Waste disposal methods:

2-Ethoxyethanol 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 2-ETHOXYETHANOL

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
6000 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 mode or continuous-flow mode.
Greater than 6000 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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of 2-ethoxyethanol; 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 6000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for 2-Ethoxyethylacetate

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: $C_2H_5OCH_2CH_2OCOCH_3$
- Synonyms: Cellosolve acetate; glycol monoethyl ether acetate; ethylene glycol monoethyl ether acetate
- Appearance and odor: Colorless liquid with a mild, non-residual odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2-ethoxyethylacetate is 100 parts of 2-ethoxyethylacetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 540 milligrams of 2-ethoxyethylacetate per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for 2-ethoxyethylacetate from 100 ppm to 50 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2-Ethoxyethylacetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

High air concentrations of 2-ethoxyethylacetate may cause irritation of the eyes and nose. The material is not very toxic when swallowed, but if a large enough dose is swallowed, death may result. It is not very toxic when inhaled in amounts likely to be encountered under ordinary conditions, but inhaling large amounts might cause vomiting, kidney damage, paralysis, and death. The material may be absorbed through the skin and, if a large amount of it is absorbed in this way, death may result.

- **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-ethoxyethylacetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2-ethoxyethylacetate 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-ethoxyethylacetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 2-ethoxyethylacetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: 2-Ethoxyethylacetate is absorbed through the skin. It also is a defatting agent and may cause dryness and cracking. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although 2-ethoxyethylacetate 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.

—Liver disease: Although 2-ethoxyethylacetate 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**

High concentrations of 2-ethoxyethylacetate vapor 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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irritating to the eyes and mucous membranes. Guinea pigs and rabbits survived exposure to saturated vapor-air mixtures (4000 ppm) for 1 hour, but two such exposures for 4 to 6 hours caused delayed death to cats.

There was narcosis before death in these animals, and damage to the kidneys was found at autopsy. This agent is absorbed through the skin. Lethal doses have been administered through the skin to rabbits. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 132
  2. Boiling point (760 mm Hg): 156 C (313 F)
  3. Specific gravity (water = 1): 0.98
  4. Vapor density (air = 1 at boiling point of 2-ethoxyethylacetate): 4.6
  5. Melting point: −62 C (−80 F)
  6. Vapor pressure at 20 C (68 F): 2 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 23
  8. Evaporation rate (butyl acetate = 1): 0.2
- **Reactivity**
  1. Conditions contributing to instability: Heat
  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 2-ethoxyethylacetate.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 47 C (117 F) (closed cup)
  2. Autoignition temperature: 380 C (716 F)
  3. Flammable limits in air, % by volume: Lower: 1.7
  4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: According to the *Handbook of Organic Industrial Solvents*, the odor of 2-ethoxyethylacetate is detectable at the threshold limit.
  2. Eye Irritation Level: According to the *Documentation of TLV's*, dogs exposed to "120 seven-hour inhalations of 600 ppm" experienced eye and nose irritation. No quantitative information is available, however, concerning the threshold of eye irritation. Patty reports that "high concentrations of vapor . . . are irritating to the eyes and nose."
  3. Evaluation of Warning Properties: Since the odor of 2-ethoxyethylacetate can be detected at the TLV, 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 2-ethoxyethylacetate 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 2-ethoxyethylacetate may be used. An analytical method for 2-ethoxyethylacetate 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 2-ethoxyethylacetate.
- Clothing wet with liquid 2-ethoxyethylacetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2-ethoxyethylacetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 2-ethoxyethylacetate, the person performing the operation should be informed of 2-ethoxyethylacetate's hazardous properties.

• Non-impervious clothing which becomes wet with 2-ethoxyethylacetate should be removed promptly and not reworn until the 2-ethoxyethylacetate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid 2-ethoxyethylacetate may contact the eyes.

SANITATION

• Skin that becomes wet with liquid 2-ethoxyethylacetate should be promptly washed or showered to remove any 2-ethoxyethylacetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2-ethoxyethylacetate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent vehicle during hot and cold spray applications of lacquers and wood stains, including automobiles, airplanes, and metal and wood finishing	Local exhaust ventilation; personal protective equipment
Use in manufacture of varnishes, thinners, lacquers, wood stains, adhesives, varnish removers, fabric coatings, paper coatings, and textile sizing	General dilution ventilation; personal protective equipment
Liberation during manufacture of cellulose acetate films, including transparent wrapping material, safety film, packaging film, and photographic film	General dilution ventilation
Liberation during coating process of fabrics, leather, and paper for water-proofing, sizing, and laminating	General dilution ventilation
Use during dipping application of lacquers and enamels of small articles having rounded or cylindrical shapes, wire flash bulbs, etc.	General dilution ventilation; personal protective equipment
Use during brushing or other hand applications of lacquers, adhesives, enamels, household cement, specialized lacquers, etc.	General dilution ventilation; personal protective equipment
Use during solvent recovery during equipment maintenance, pouring solvent, and refilling containers	General dilution ventilation; personal protective equipment
Use as a solvent for many oils and gums	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 2-ethoxyethylacetate 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 2-ethoxyethylacetate gets on the skin, promptly flush the contaminated skin with water. If 2-ethoxyethylacetate 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 2-ethoxyethylacetate, 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-ethoxyethylacetate 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 2-ethoxyethylacetate 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. 2-Ethoxyethylacetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

2-Ethoxyethylacetate 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: "2-Ethoxyethylacetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR 2-ETHOXYETHYLACETATE (CELLOSOLVE ACETATE)

Condition	Minimum Respiratory Protection* *Required Above 100 ppm*
Vapor Concentration	
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.*
Greater than 2500 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 Ethyl Acetate

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: $CH_3COOC_2H_5$
- Synonyms: Acetic ester; acetic ether; ethyl ethanoate
- Appearance and odor: Colorless liquid with a pleasant, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl acetate is 400 parts of ethyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1400 milligrams of ethyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ethyl acetate may cause irritation of the eyes, nose, and throat. Severe overexposure may cause weakness, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure may produce 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 ethyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl acetate 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 ethyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Ethyl acetate 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 ethyl acetate 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 ethyl acetate 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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl acetate vapor is irritating to the eyes and respiratory passages of man at concentrations above 400 ppm. In animals it has a narcotic effect at concentrations of over 5000 ppm. Due to its irritating properties, employees will not voluntarily remain in such high concentrations. Repeated exposures of rabbits to 4450 ppm for 1 hour daily for 40 days resulted in anemia with leukocytosis, and damage to liver and kidneys. Animals exposed to lethal concentrations died with pulmonary edema

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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 hemorrhage. This substance is a defatting agent, and prolonged exposure may cause irritation of the skin. Painful conjunctival irritation may occur from splashes in the eye. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 88
  2. Boiling point (760 mm Hg): 77 C (171 F)
  3. Specific gravity (water = 1): 0.9
  4. Vapor density (air = 1 at boiling point of ethyl acetate): 3.0
  5. Melting point: −83 C (−117 F)
  6. Vapor pressure at 20 C (68 F): 76 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 8.7
  8. Evaporation rate (butyl acetate = 1): 6
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, or 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 ethyl acetate.
  4. Special precautions: Ethyl acetate will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −4.4 C (24 F) (closed cup)
  2. Autoignition temperature: 427 C (800 F)
  3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 11
  4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical
- **Warning properties**
  1. Odor Threshold: May and Summer report odor thresholds for ethyl acetate of 0.0056 ppm and 50 ppm, respectively.
  2. Eye Irritation Level: Grant states that "a concentration of 400 ppm in air causes a sensation of irritation in human eyes." Animals exposed to much higher concentrations developed no corneal damage, only conjunctival irritation.
  3. Evaluation of Warning Properties: Through its odor and irritant effects, ethyl acetate can be detected below or at the permissible exposure limit. For the purposes of this guideline, ethyl acetate 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 ethyl acetate 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 ethyl acetate may be used. An analytical method for ethyl acetate 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 ethyl acetate.
- Clothing wet with liquid ethyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl acetate, the person performing the operation should be informed of ethyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid ethyl acetate should be removed immediately and not reworn until the ethyl acetate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl acetate may contact the eyes.

SANITATION

• Skin that becomes wet with liquid ethyl acetate should be promptly washed or showered to remove any ethyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use of shellacs, lacquers, dopes, varnishes, and stains	Local exhaust ventilation; general dilution ventilation
Liberation during manufacture of smokeless powder; during manufacture of artificial leather; during preparation of photographic films	Process enclosure; general dilution ventilation
Liberation and use as a solvent during application of coatings containing nitrocellulose, cellulose acetate, shellac, synthetic rubber, vinyl resins, and inks	Process enclosure; general dilution ventilation
Use as a cleaning agent in textile industry	Process enclosure; general dilution ventilation
Liberation during manufacture of photographic film	Process enclosure; general dilution ventilation
Liberation during manufacture of linoleum and plastic wood; during manufacture of dyes, drug intermediates, ethyl acetoacetate, etc.; during use of duplicator fluid	Process enclosure; general dilution ventilation
Liberation during use of varnish removers	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 ethyl acetate 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 ethyl acetate gets on the skin, promptly flush the contaminated skin with water. If ethyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of ethyl acetate, 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 ethyl acetate 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 ethyl acetate 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. Ethyl acetate should not be allowed

to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Ethyl acetate 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.

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RESPIRATORY PROTECTION FOR ETHYL ACETATE

Condition	Minimum Respiratory Protection* Required Above 400 ppm
Vapor Concentration	
1000 ppm or less	Any 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 Health Guideline for Ethyl Acrylate

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: $CH_2=CHCOOC_2H_5$
- Synonyms: Ethyl propenoate
- Appearance and odor: Colorless liquid with a sharp, acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl acrylate is 25 parts of ethyl acrylate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 100 milligrams of ethyl acrylate 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 ethyl acrylate from 25 ppm to 5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl acrylate can affect the body if it is inhaled, comes in contact with the eyes or skin., or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ethyl acrylate may cause irritation of the eyes, nose, throat, and lungs. Death may be caused by lung damage from breathing high air levels or from swallowing it.

2. Long-term Exposure: Prolonged contact with the skin or eyes may result in severe damage.

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 ethyl acrylate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl acrylate 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 ethyl acrylate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl acrylate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Ethyl acrylate is absorbed through the skin. It also is a defatting agent and may cause dryness or cracking. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although ethyl acrylate 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 ethyl acrylate is not known as a kidney toxin in humans, the importance of this organ in the excretion of certain chemicals and their metabolites should be considered before exposing persons with impaired kidney function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The vapor of ethyl acrylate is irritating to the conjunctiva and upper respiratory tract. In moderate concentrations there are characteristic lacrimatory effects in man. Animals exposed to high concentrations show marked

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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irritation of the eyes and of the respiratory tract, leading to pulmonary edema. The lowest concentration of vapor producing no significant effect in rodents is 75 ppm. A concentration of 2000 ppm vapor killed rats in 4 hours, with death attributable to severe pulmonary irritation, although 1000 ppm for 4 hours allowed survival. Prolonged contact with the skin in animals causes moderate damage, and skin sensitization may occur. Fatal doses are absorbed through the skin of animals exposed for 24 hours. While there are no reports of injury to man from long-term exposure to concentrations ordinarily encountered in the work situation, common practice suggests that most workmen do not tolerate exposure to 25 ppm for more than a few minutes.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): 99 C (211 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of ethyl acrylate): 3.45
5. Melting point: −75 C (−103 F)
6. Vapor pressure at 20 C (68 F): 29.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
8. Evaporation rate (butyl acetate = 1): 3.3

- **Reactivity**

1. Conditions contributing to instability: Heat and/or lack of appropriate inhibitor concentration can cause ethyl acrylate to polymerize violently and burst container.
2. Incompatibilities: Contact with oxidizing materials, including peroxides and other initiators of polymerization, strong alkalies, and atmospheric moisture may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl acrylate.
4. Special precautions: Inhibitors do not function in absence of air, so inert gas blankets should not be used.

- **Flammability**

1. Flash point: 9 C (48 F) (closed cup)
2. Autoignition temperature: 383 C (721 F)
3. Flammable limits in air, % by volume: Lower: 1.8
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor of ethyl acrylate vapor is readily detectable at 1 ppm and was described as fairly strong and moderately irritating at 4 ppm." The Manufacturing Chemists Association reports that an odor of ethyl acrylate can be detected by most persons at 8 ppm.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "a concentration of 272 ppm ethyl acrylate vapor caused irritation of the conjunctiva of rabbit eyes, but 75 ppm did not elicit any observable reaction." According to the MCA, however, irritation of the eyes occurs at about 75 ppm.
3. Other Information: The MCA states that irritation of the mucous membranes occurs at 75 ppm.

The AIHA *Hygienic Guide* states that the TLV (25 ppm) "is considered to be too high to prevent irritating effects in humans."

4. Evaluation of Warning Properties: Through its odor ethyl acrylate can be detected below the permissible exposure limit, and through its irritant effects it can be detected at or just several times above the TLV. Therefore, the substance is considered to have 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 ethyl acrylate 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 ethyl acrylate may be used. An analytical method for ethyl acrylate 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 ethyl acrylate.

• Clothing wet with liquid ethyl acrylate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl acrylate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl acrylate, the person performing the operation should be informed of ethyl acrylate's hazardous properties.

• Where exposure of an employee's body to liquid ethyl acrylate 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 liquid ethyl acrylate or non-impervious clothing which becomes contaminated with liquid ethyl acrylate should be removed immediately and not reworn until the ethyl acrylate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl acrylate may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid ethyl acrylate should be promptly washed or showered with soap or mild detergent and water to remove any ethyl acrylate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl acrylate may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of acrylic resins for use in paint formulations, industrial coatings, and latexes; use in manufacture of plastics such as ethylene ethyl acrylate	Local exhaust ventilation; personal protective equipment
Use in manufacture of polyacrylate elastomers and acrylic rubber	Local exhaust ventilation; personal protective equipment
Use in forming of denture materials	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 ethyl acrylate 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 ethyl acrylate gets on the skin, immediately flush the contaminated skin with water. If ethyl acrylate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of ethyl acrylate, 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 ethyl acrylate 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 ethyl acrylate 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. Ethyl acrylate should not be allowed

to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Ethyl acrylate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill in an area where the odor will not be objectionable.

2. By atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR ETHYL ACRYLATE

Condition	Minimum Respiratory Protection* Required Above 25 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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ethyl acrylate; 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 2000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Ethylamine

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: $C_2H_5NH_2$
- Synonyms: Ethylamine, anhydrous; aminoethane; monoethylamine
- Appearance and odor: Colorless liquid or gas with a strong, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethylamine is 10 parts of ethylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 18 milligrams of ethylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethylamine 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**

1. Short-term Exposure: Ethylamine causes severe irritation of the eyes and skin. It may also cause irritation of the nose, throat, and lungs.

2. Long-term Exposure: Repeated or prolonged exposure to ethylamine may also cause irritation of the lungs and kidney damage.

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 ethylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethylamine 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 ethylamine exposure.

—Chronic respiratory disease: Ethylamine causes lung irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethylamine might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: Ethylamine is an eye irritant and has caused corneal edema in workers. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Skin disease: Ethylamine is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although ethylamine 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 ethylamine 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.

—Cardiovascular disease: Ethylamine causes myocardial degeneration in animals. Persons with cardiac disease may be at increased risk.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethylamine vapor is a primary irritant to mucous membranes, eyes, and skin. Exposure to 8000 ppm for 4 hours was lethal to rats. Rabbits survived exposures to

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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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50 ppm daily for 6 weeks but showed pulmonary irritation and some myocardial degeneration; corneal damage was observed after 2 weeks of exposure. In the rabbit eye, 1 drop of a 70% solution of ethylamine caused immediate, severe irritation. Eye irritation and corneal edema in humans have been reported from industrial exposure. A 70% solution of the base dropped on the skin of guinea pigs caused prompt skin burns leading to necrosis; when held in contact with guinea pig skin for 24 hours there was severe skin irritation with extensive necrosis and deep scarring.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 45.1
2. Boiling point (760 mm Hg): 16.7 C (62 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of ethylamine): 1.6
5. Melting point: −81 C (−114 F)
6. Vapor pressure at 20 C (68 F): 1.18 atmospheres
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid ethylamine with strong acids will cause violent spattering. 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 in a fire involving ethylamine.
4. Special precautions: Liquid ethylamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Less than −18 C (less than 0 F) (closed cup)
2. Autoignition temperature: 385 C (725 F)
3. Flammable limits in air, % by volume: Lower: 3.5; Upper: 14.0
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No quantitative data are available concerning the odor threshold of ethylamine.
2. Eye Irritation Level: Patty and the *Documentation of TLV's* report that in repeated exposure experiments, "100 ppm ethylamine produced irritation of the cornea" in rabbits. In addition, corneal injury, which did not appear for 2 weeks, was produced in rabbits exposed repeatedly to 50 ppm ethylamine. This concentration (50 ppm) is not specifically stated to be the lowest concentration producing eye injury.
3. Other Information: Patty and the *Documentation of TLV's* report that rabbits exposed to both 100 ppm and 50 ppm ethylamine for 7 hours per day, 5 days per week for 6 weeks, experienced lung irritation.
4. Evaluation of Warning Properties: Since no information is available concerning the odor threshold of ethylamine, and since the irritant effects produced by this substance are not stated to occur immediately upon exposure, ethylamine is treated as a substance 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 ethylamine in an adsorption tube containing silica gel, followed by desorption with sulfuric acid and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethylamine may be used. An analytical method for ethylamine 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 ethylamine, where skin contact may occur.

• Clothing wet with liquid ethylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethylamine, the person performing the operation should be informed of ethylamine's hazardous properties.

• Where exposure of an employee's body to liquid ethylamine 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 ethylamine should be removed immediately and not reworn until the ethylamine is removed from the clothing.

• Any clothing which becomes wet with liquid ethylamine should be removed immediately and not reworn until the ethylamine 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 ethylamine or solutions containing ethylamine contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid ethylamine or solutions containing 0.75% or more of ethylamine by weight, an eyewash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with ethylamine should be immediately washed or showered to remove any ethylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of agricultural chemicals for herbicides; use as a dyestuff intermediate; use as a solvent for dyes, resins, and oils; use as a catalyst for polyurethane foams; use in pharmaceuticals, emulsifying agents, and as a vulcanization accelerator for sulfur-cured rubbers	General dilution ventilation; local exhaust ventilation
Use as a stabilizer for rubber latex; use as a catalyst for curing epoxy resins	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in synthesis of dimethylolethyltriazone, a wash and wear agent for cotton fabrics; synthesis of 1,3-diethylthiourea, a corrosion inhibitor	General dilution ventilation; local exhaust ventilation
Use in synthesis of chemical intermediates and solvents; use as plasticizers and in refining of lubricating oils	General dilution ventilation; local exhaust ventilation
Use as a selective solvent in refining of petroleum and vegetable oils	General dilution ventilation
Use in synthesis of alkyl isocyanates for intermediates in manufacture of organic products such as pharmaceuticals and resins	General dilution ventilation; local exhaust ventilation
Use in synthesis of rhodamine dyes	General dilution ventilation; local exhaust ventilation
Use as a deflocculating agent in ceramics industry; use in manufacture of detergents	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 ethylamine or solutions containing ethylamine 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 ethylamine gets on the skin, immediately flush the contaminated skin with water. If ethylamine soaks 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 ethylamine, 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 ethylamine has 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 LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

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

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Allow ethylamine to evaporate. Ethylamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• 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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• U.S. Coast Guard: "Ethylamine," *Characteristics of Liquid Chemicals Proposed for Bulk Water Movement.*

RESPIRATORY PROTECTION FOR ETHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
4000 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 4000 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 ethylamine. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Ethyl Benzene

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: $C_2H_5C_6H_5$
- Synonyms: Phenylethane; ethylbenzol
- Appearance and odor: Colorless liquid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl benzene is 100 parts of ethyl benzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 435 milligrams of ethyl benzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl benzene 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: Ethyl benzene causes irritation of the eyes, nose, throat, and skin. With exposure to high concentrations, irritating effects are more pronounced, and a person may begin to feel weak, dizzy, drowsy, and become unconscious.

2. Long-term Exposure: Prolonged or repeated ethyl benzene exposure of the skin may casue 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 ethyl benzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl benzene 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 ethyl benzene exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl benzene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Kidney disease: Although ethyl benzene 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 ethyl benzene 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: Ethyl benzene 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**

Ethyl benzene is primarily an irritant of skin and, to some degree, of eyes and upper respiratory tract. Systemic absorption causes depression of the central nervous system with narcosis at very high concentrations. Aspiration of small amounts causes extensive edema and hemorrhage of lung tissue. It is readily metabolized and excreted chiefly as mandelic acid in the urine.

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

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 106
  2. Boiling point (760 mm Hg): 136 C (277 F)
  3. Specific gravity (water = 1): 0.865
  4. Vapor density (air = 1 at boiling point of ethyl benzene): 3.66
  5. Melting point: −95 C (−139 F)
  6. Vapor pressure at 20 C (68 F): 7.1 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 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 ethyl benzene.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 15 C (59 F) (closed cup)
  2. Autoignition temperature: 432 C (810 F)
  3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 6.7
  4. Extinguishant: Dry chemical, foam, or carbon dioxide
- **Warning properties**
  1. Odor Threshold: According to the Department of Transportation's *CHRIS Hazardous Chemical Data*,, ethyl benzene has an odor threshold of 140 ppm.
  2. Eye Irritation Level: According to the AIHA *Hygienic Guide*, "the vapor caused a noticeable eye irritation in humans at concentrations of 200 ppm."
  3. Evaluation of Warning Properties: Through its odor and irritant effects, ethyl benzene can be detected at a concentration less than twice the permissible exposure limit. Therefore, for the purposes of this guideline, ethyl benzene 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 ethyl benzene 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 ethyl benzene may be used. An analytical method for ethyl benzene 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 ethyl benzene.
- Clothing wet with liquid ethyl benzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl benzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl benzene, the person performing the operation should be informed of ethyl benzene's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid ethyl benzene should be removed promptly and not reworn until the ethyl benzene is removed from the clothing.
- Any clothing which becomes wet with liquid ethyl benzene should be removed immediately and not reworn until the ethyl benzene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl benzene may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid ethyl benzene should be promptly washed or showered with soap or mild detergent and water to remove any ethyl benzene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl benzene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture of styrene monomer	Local exhaust ventilation
Use during spray application of vinyl resin surface coating	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of paints, varnishes, and other surface coatings	Local exhaust ventilation; general dilution ventilation
Use in manufacture and application of rubber adhesives	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use during electroplating of aluminum on copper or steel	Local exhaust ventilation for open-surface tanks
Liberation during oven baking and drying of surface coatings	Local exhaust ventilation for ovens
Liberation during application of surface coatings by dipping, flow coatings, and roller coating	Local exhaust ventilation
Liberation during use as an intermediate in dye manufacture	General dilution ventilation
Use as a heat-transfer medium; use as a dielectric	General dilution ventilation; personal protective equipment
Liberation during production of acetophenone by oxidation of ethyl benzene	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 ethyl benzene 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 ethyl benzene gets on the skin, promptly flush the contaminated skin with water. If ethyl benzene 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 ethyl benzene, 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 ethyl benzene 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 ethyl 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, 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. Ethyl benzene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Ethyl benzene 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

• American Conference of Governmental Industrial Hygienists: "Ethyl Benzene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR ETHYL BENZENE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
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 Health Guideline for Ethyl Bromide

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_5Br
- Synonyms: Bromoethane
- Appearance and odor: Colorless to yellow liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl bromide is 200 parts of ethyl bromide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 890 milligrams of ethyl bromide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl bromide 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 ethyl bromide may cause irritation of the lungs, eyes, and skin. It may cause dizziness, loss of balance, slurred speech, unconsciousness, and death. Overexposure to this agent may also cause damage to the liver, kidneys, and heart. After-effects from severe exposure may occur up to 30 hours after the exposure has ceased.

- **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 ethyl bromide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl bromide 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 ethyl bromide exposure.

—Skin disease: Ethyl bromide can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Ethyl bromide has produced liver damage in animals and man, which should be considered before exposing persons with impaired liver function.

—Kidney disease: Since ethyl bromide has produced kidney damage in animals and man, special consideration in those with impaired renal function is justified.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl bromide might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of ethyl bromide might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl bromide vapor is a respiratory irritant, a narcotic, and a hepato- and renal toxin. Exposure of guinea pigs for 30 minutes to 2.4% by volume (24,000 ppm) was fatal within 3 days due to pulmonary congestion, centrolobular necrosis of the liver, and diffuse nephritis; exposure to 3200 ppm for 9 hours produced lung irritation and nephritis; death occurred after 1 to 5 days.

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 former use of ethyl bromide as a human anesthetic produced respiratory irritation and caused some fatalities, either immediately, due to respiratory or cardiac arrest, or delayed, from effects on the liver, kidney, or heart. Relatively little experience with this substance in industry has been reported, but exposure of volunteers to 6500 ppm for 5 minutes produced vertigo, slight headache, and mild eye irritation. Irritation of the skin occurs from repeated contact with ethyl bromide liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 109
2. Boiling point (760 mm Hg): 38.8 C (100 F)
3. Specific gravity (water = 1): 1.45
4. Vapor density (air = 1 at boiling point of ethyl bromide): 3.8
5. Melting point: −119 C (−182 F)
6. Vapor pressure at 20 C (68 F): 375 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: Contact with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl bromide. Ethyl bromide readily decomposes into hydrogen bromide and bromine particularly in the presence of hot surfaces.
4. Special precautions: Liquid ethyl bromide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Less than −20 C (less than −4F) (closed cup)
2. Autoignition temperature: 511 C (952 F)
3. Flammable limits in air, % by volume: Lower: 6.7; Upper: 11.3
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

Since the AIHA *Hygienic Guide* states that the odor of ethyl bromide is detectable only at concentrations well above the permissible exposure, it has been treated as a substance with poor warning properties. In addition, the *Hygienic Guide* reports a situation in which only mild eye irritation was produced in a human subject after a 5-minute exposure to 6500 ppm, a concentration many times greater than the permissible exposure. Information on the eye irritation threshold is not available.

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 ethyl bromide vapors using an adsorption tube with subsequent desorption with isopropyl alcohol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl bromide may be used. An analytical method for ethyl bromide 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 ethyl bromide.

• Clothing contaminated with liquid ethyl bromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl bromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl bromide, the person performing the operation should be informed of ethyl bromide's hazardous properties.

• Any clothing which becomes wet with liquid ethyl bromide should be removed immediately and not reworn until the ethyl bromide is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl bromide may contact the eyes.

SANITATION

• Skin that becomes wet with liquid ethyl bromide should be promptly washed or showered with soap or mild detergent and water to remove any ethyl bromide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl bromide may occur and control methods which may be effective in each case:

Operation	Controls
Use as an alkylating or ethylating agent in manufacture of pharmaceuticals, and to a lesser extent, chemicals, dyes, and perfumes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for fats, waxes, and resins	Process enclosure; if possible, local exhaust ventilation; personal protective equipment
Use as a local surface anesthetic for minor surgery and neuralgic pain	General dilution ventilation
Use as a liquid fumigant for grain and fruit	General dilution ventilation; personal protective equipment
Liberation during use as a refrigerant	Process enclosure; 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 ethyl bromide 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 ethyl bromide gets on the skin, promptly flush the contaminated skin using soap or mild detergent and water. If ethyl bromide soaks through the clothing, remove the clothing promptly and flush 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 ethyl bromide, 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 ethyl bromide 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 ethyl bromide 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. Ethyl bromide 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 ethyl bromide vapors are permitted.

• Waste disposal method:

Ethyl bromide may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Ethyl Bromide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR ETHYL BROMIDE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3500 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 with a half facepiece operated in pressure-demand or other positive pressure or 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 Health Guideline for Ethyl Butyl Ketone

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: $C_2H_5COC_4H_9$
- Synonyms: Butyl ethyl ketone; 3-heptanone
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl butyl ketone is 50 parts of ethyl butyl ketone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 230 milligrams of ethyl butyl ketone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl butyl ketone 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: Ethyl butyl ketone may cause irritation of the eyes, nose, throat, and lungs. Exposure to high concentrations may cause headaches, dizziness, or unconsciousness.

2. Long-term Exposure: Prolonged or repeated skin contact may cause dryness and 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 ethyl butyl ketone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl butyl ketone 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 ethyl butyl ketone exposure.

—Kidney disease: Although ethyl butyl ketone 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 ethyl butyl ketone might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although ethyl butyl ketone 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: Ethyl butyl ketone 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**

There is some local irritation of the skin and respiratory tract by solvent effect of ethyl butyl ketone on lipids. Central nervous depression occurs on exposure to high concentration, producing narcosis. Effects may be more pronounced in unacclimated individuals. No chronic systemic effects have been 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.

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: 114
  2. Boiling point (760 mm Hg): 147 C (297 F)
  3. Specific gravity (water = 1): 0.82
  4. Vapor density (air = 1 at boiling point of ethyl butyl ketone): 3.93
  5. Melting point: −39 C (−38 F)
  6. Vapor pressure at 20 C (68 F): 4 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.43
  8. Evaporation rate (butyl acetate = 1): 0.45
- **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 ethyl butyl ketone.
  4. Special precautions: Ethyl butyl ketone will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 46 C (115 F) (open cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: 1.4; Upper: 8.8
  4. Extinguishant: Carbon dioxide, dry chemical, or foam
- **Warning properties**
  1. Odor Threshold: According to Patty, ethyl butyl ketone has a "typical ketone-type odor."
  2. Eye Irritation Level: According to the *Documentation of TLV's*, "when in contact with skin and eyes, it (ethyl butyl ketone) produces, at most, irritation of mild degree."
  3. Evaluation of Warning Properties: For the purposes of this guideline, ethyl butyl ketone 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 ethyl butyl ketone 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 ethyl butyl ketone may be used. An analytical method for ethyl butyl ketone 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 ethyl butyl ketone.
- Clothing wet with liquid ethyl butyl ketone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl butyl ketone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl butyl ketone, the person performing the operation should be informed of ethyl butyl ketone's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid ethyl butyl ketone should be removed promptly and not reworn until the ethyl butyl ketone is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl butyl ketone may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid ethyl butyl ketone should be promptly washed or showered to remove any ethyl butyl ketone.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl butyl ketone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during application of lacquers, varnishes, epoxies, vinyl coatings, finishes, and adhesives	Local exhaust ventilation; personal protective equipment
Liberation during application of lacquer, varnishes, epoxies, vinyl coatings, finishes, and adhesives by dipping, roller coating, tumbling, knifing, or brushing	Local exhaust ventilation; general dilution ventilation
Liberation during oven or air drying of coatings and adhesives	General dilution ventilation
Use during manual application of cellulosic, acetate, and rubber adhesives in shoe manufacturing, book binding, and packaging	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use of cellulosic household cements	General dilution ventilation
Liberation during application of mastics or other natural gum/ based adhesives for floor and wall tiles, other floor coverings, automobile silencer, and lining pads	General dilution ventilation; local exhaust ventilation
Liberation during cleaning and maintenance of ketone-processing equipment, such as distillation columns, reactors, mixers, and storage vessels	Personal protective equipment
Liberation during blending of coating and adhesive raw materials in open mixers	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 ethyl butyl ketone 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 ethyl butyl ketone gets on the skin, promptly flush the contaminated skin with water. If ethyl butyl ketone soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is evidence of skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of ethyl butyl ketone, 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 ethyl butyl ketone 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 ethyl butyl ketone 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. Ethyl butyl ketone 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 ethyl butyl ketone vapors are permitted.

• Waste disposal methods:

Ethyl butyl ketone 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.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Ethyl Butyl Ketone," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.

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• Smyth, H. F., et al.: "Range-Finding Toxicity Data, List III," *Journal of Industrial Hygiene*, 31:1, pp. 60-62, 1949.

• Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – 3-Heptanone*, New York, 1969.

RESPIRATORY PROTECTION FOR ETHYL BUTYL KETONE

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).**
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.
3000 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 3000 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.

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

**If eye irritation occurs, a full-facepiece respirator should be worn.

Occupational Health Guideline for Ethyl Chloride

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_5Cl
- Synonyms: Chloroethane; monochloroethane; hydrochloric ether; muriatic ether
- Appearance and odor: Colorless liquid or gas with a pungent, ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl chloride is 1000 parts of ethyl chloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2600 milligrams of ethyl chloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl chloride can affect the body if it is inhaled, if it comes in contact with the eyes or skin. or if it is swallowed. In the liquid form, it may be absorbed through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Ethyl chloride may cause drowsiness, unconsciousness, irregular heart beat, and death. It may also cause irritation of the eyes and abdominal cramps. Spilled on the skin, it may cause frostbite.

2. Long-term Exposure: Ethyl chloride may cause liver and kidney damage.

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 ethyl chloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl chloride 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 ethyl chloride exposure.

—Liver disease: Ethyl chloride is known as a liver toxin in animals and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Ethyl chloride is known as a kidney toxin in animals and justifies special consideration before exposing persons with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl chloride might cause exacerbation of symptoms due to its irritant properties.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of ethyl chloride might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl chloride vapor is a narcotic. Guinea pigs died from a 9-hour exposure to 40,000 ppm but survived 4-½ hour exposure; histopathological changes in the lungs, liver, and kidneys were observed in animals in the latter group. Inhalation of 40,000 ppm by human subjects caused dizziness, eye irritation, and abdominal cramps, while inhalation of 3.36% by volume (33,600 ppm) caused a toxic effect after 30 seconds, increasing within 5 minutes to noisy talkativeness followed by incoordina-

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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tion. At 2.5% by volume (25,000 ppm) there was incoordination; 1.9% (19,000 ppm) caused weak analgesia after 12 minutes, and 1.3% (13,000 ppm) caused slight symptoms of inebriation. Sudden and unforeseen fatalities from ethyl chloride anesthesia have been reported, probably due to respiratory or cardiac arrest. Chronic effects from industrial exposure have not been reported, although skin absorption is said to occur. In liquid form this substance may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 64.5
2. Boiling point (760 mm Hg): 12.2 C (54 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of ethyl chloride): 2.2
5. Melting point: −139 C (−218 F)
6. Vapor pressure at 20 C (68 F): 1064 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.57
8. Evaporation rate (butyl acetate = 1): Much higher than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving ethyl chloride.
4. Special precautions: Liquid ethyl chloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −50 C (−58 F) (closed cup)
2. Autoignition temperature: 519 C (966 F)
3. Flammable limits in air, % by volume: Lower: 3.8; Upper: 15.4
4. Extinguishant: Stop flow of gas. Use carbon dioxide, dry chemical, or foam for small fires.

- **Warning properties**

Ethyl chloride has a somewhat pungent, ether-like odor, but no quantitative data are available on the odor threshold. For the purposes of this guideline, therefore, ethyl chloride has been treated as a material with poor warning properties.

Ethyl chloride is a mild eye irritant. Grant reports that at 4% the gas has been noted to cause slight irritation of the eyes of human beings.

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 ethyl chloride 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 repeated or prolonged skin contact with liquid ethyl chloride.
- Clothing wet with liquid ethyl chloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl chloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl chloride, the person performing the operation should be informed of ethyl chloride's hazardous properties.
- Any clothing which becomes wet with liquid ethyl chloride should be removed immediately and not reworn until the ethyl chloride has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl chloride may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use in production of tetraethyl lead and ethyl cellulose	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a local or general anesthetic; use as a refrigeration compound; use as a solvent for fats, oils, waxes, phosphorus, acetylene, and many resins	General dilution ventilation; personal protective equipment
Use in organic synthesis of perchloroethane, esters, and Grignard reagents	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of dyes and drugs; use as a propellant in aerosols	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of perfumes	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 liquid ethyl chloride 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 liquid ethyl chloride gets on the skin, promptly wash the contaminated skin with water if the ethyl chloride has not already evaporated. If liquid ethyl chloride soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of ethyl chloride, 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 ethyl chloride 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 ethyl chloride 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 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 reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Ethyl chloride should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
4. If in the gaseous form, stop flow of gas.

• Waste disposal methods:

Ethyl chloride may be disposed of:

1. If in the liquid form, by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. If in the gaseous form, by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Ethyl Chloride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
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RESPIRATORY PROTECTION FOR ETHYL CHLORIDE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
20,000 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 with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 20,000 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 Ethylene Chlorohydrin

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_2ClCH_2OH
- Synonyms: 2-Chloroethanol; 2-chloroethyl alcohol
- Appearance and odor: Colorless liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethylene chlorohydrin is 5 parts of ethylene chlorohydrin per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 16 milligrams of ethylene chlorohydrin per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for ethylene chlorohydrin a Threshold Limit Value of 1 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethylene chlorohydrin can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may be absorbed through the skin without causing irritation.

- **Effects of overexposure**

Exposure to ethylene chlorohydrin vapor may cause irritation of the eyes, nose, throat, and lungs, nausea, vomiting, dizziness, poor coordination, numbness, visual disturbance, liver or kidney damage (lower concentrations may cause serious effects without causing irritation). Breathing in higher concentrations produces headache, thirst, delirium, low blood pressure, collapse, and unconsciousness. The urine may contain blood. Death may occur from lung or brain damage. Absorption through the skin can cause the above symptoms without skin irritation. Prolonged overexposure to ethylene chlorohydrin may cause the skin to become yellow and a change in frequency of urination or the amount of urine.

- **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 ethylene chlorohydrin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethylene chlorohydrin 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, and central nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Ethylene chlorohydrin may cause liver damage. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has 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 a semi-annual basis for the first two years and annually thereafter.

- **Summary of toxicology**

Ethylene chlorohydrin vapor is highly toxic to the liver, kidneys, brain, and other organs. It is rapidly absorbed through the skin. A concentration of 250 ppm was fatal to rats in 4 hours; 125 ppm was not. A human fatality was reported following exposure to an estimat-

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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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ed 300 ppm for 2-¼ hours. In another fatal case, autopsy showed severe damage to the liver and brain. Several employees survived exposures averaging 18 ppm but showed signs of circulatory shock with incoordination and repeated vomiting. There is little margin of safety between early reversible symptoms and fatal intoxication. Absorption by any route, including the skin, may lead to severe illness or death. Contact with vapor causes irritation of mucous membranes, nausea, vomiting, vertigo, incoordination, numbness, and visual disturbance. With higher concentrations, headache, severe thirst, delirium, low blood pressure, collapse, shock, and coma may result. Urine may contain albumin, casts, and red blood cells. Death results from pulmonary edema or from congestion and edema of the brain. The cause of the toxic effect is probably the result of oxidation of the alcohol to chloracetic acid. The liquid instilled in rabbit eyes caused moderately severe injury, but in human eyes corneal burns have been observed to recover within 48 hours. Skin contact is particularly hazardous, because there are no signs of immediate irritation to warn the victim of exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 80.5
2. Boiling point (760 mm Hg): 130 C (266 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of ethylene chlorohydrin): 2.8
5. Melting point: −62.6 C (−81 F)
6. Vapor pressure at 20 C (68 F): 5 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 strong oxidizers may cause fires and explosions. Contact with strong caustics may cause formation of flammable ethylene gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving ethylene chlorohydrin.
4. Special precautions: Ethylene chlorohydrin will attack some forms of plastics, rubber, and coatings. Special attention to the care and maintenance of personal protective equipment should be maintained.

- **Flammability**

1. Flash point: 60 C (140 F) (closed cup)
2. Autoignition temperature: 425 C (797 F)
3. Flammable limits in air, % by volume: Lower: 4.9; Upper: 15.9
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

- **Warning properties**

According to the AIHA *Hygienic Guide*, the warning properties of ethylene chlorohydrin are "poor and inadequate to prevent injury."

Ethylene chlorohydrin is an eye irritant, according to the *Hygienic Guide*.

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 ethylene chlorohydrin vapors using an adsorption tube with subsequent desorption with isopropyl alcohol 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 ethylene chlorohydrin may be used. An analytical method for ethylene chlorohydrin 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 ethylene chlorohydrin.

• Clothing contaminated with liquid ethylene chlorohydrin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethylene chlorohydrin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethylene chlorohydrin, the person performing the operation should be informed of ethylene chlorohydrin's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid ethylene chlorohydrin, 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 liquid ethylene chlorohydrin should be removed immediately and not reworn until the ethylene chlorohydrin 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 ethylene chlorohydrin contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid ethylene chlorohydrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid ethylene chlorohydrin should be immediately washed or showered to remove any ethylene chlorohydrin.

• Eating and smoking should not be permitted in areas where liquid ethylene chlorohydrin is handled, processed, or stored.

• Employees who handle liquid ethylene chlorohydrin 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 ethylene chlorohydrin may occur and control methods which may be effective in each case:

Operation	Controls
Use as a fumigant in treatment of seed potatoes	General dilution ventilation; personal protective equipment
Use in dyeing operations during color printing of textiles	Process enclosure; local exhaust ventilation
Use during cleaning, degreasing, and dewaxing operations	Material substitution; process enclosure; local exhaust ventilation
Use in organic synthesis and synthesis of dyes, pharmaceuticals, and resin processing; use in extraction of pine lignin and oil of rose	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 ethylene chlorohydrin 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 ethylene chlorohydrin gets on the skin, immediately flush the contaminated skin with water. If ethylene chlorohydrin soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of ethylene chlorohydrin, 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 ethylene chlorohydrin 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 ethylene chlorohydrin 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. Ethylene chlorohydrin should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Ethylene chlorohydrin 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.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Ethylene Chlorohydrin," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR ETHYLENE CHLOROHYDRIN

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ethylene chlorohydrin; 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 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Ethylenediamine

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: $NH_2CH_2CH_2NH_2$
- Synonyms: 1,2-Diaminoethane; ethylenediamine, anhydrous; 1,2-ethanediamine
- Appearance and odor: Colorless liquid or solid with an ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethylenediamine is 10 parts of ethylenediamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 25 milligrams of ethylenediamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethylenediamine 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**

1. Short-term Exposure: Ethylenediamine vapors may cause irritation of the eyes, nose, and throat. If splashed on the skin, it may cause severe irritation, skin damage, and blistering. If splashed in the eyes, it may cause damage. It may cause tingling of the face.

2. Long-term Exposure: Repeated or prolonged overexposure to ethylenediamine may cause dermatitis. A person may become allergic to ethylenediamine (skin rash and asthma). Liver, kidney, and lung damage may occur from repeated exposure to this chemical.

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 ethylenediamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethylenediamine 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 ethylenediamine would be expected to be at increased risk from exposure. Examination of the respiratory system, liver, and kidneys 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**

Ethylenediamine vapor is a sensitizer and primary irritant to the skin, mucous membranes, and respiratory tract. Exposure of rats to 4000 ppm for 8 hours was uniformly fatal as a result of kidney injury, although some lung injury also occurred; 2000 ppm was not lethal. Rats exposed daily for 30 days to 484 ppm did not survive; injury to lungs, liver, and kidneys was observed; at 132 ppm there was no mortality. In human subjects, inhalation of 400 ppm for 5 to 10 seconds caused intolerable nasal irritation; 200 ppm caused tingling of the face and slight nasal irritation; 100 ppm was not irritating. In the eye of a rabbit the liquid caused extreme irritation and corneal damage; partial corneal opacity was produced by a 5% solution. The undiluted liquid applied to the shaved skin of rabbits and left uncovered produced severe irritation and ne-

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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crosis. Cutaneous sensitization in man has been observed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 60.1
  2. Boiling point (760 mm Hg): 117 C (242 F)
  3. Specific gravity (water = 1): 0.91
  4. Vapor density (air = 1 at boiling point of ethylenediamine): 2.1
  5. Melting point: 11 C (52 F)
  6. Vapor pressure at 20 C (68 F): 10 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): 0.91
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact of liquid ethylenediamine with strong acids will cause violent spattering. Contact with strong oxidizers and chlorinated organic compounds 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 ethylenediamine.
  4. Special precautions: Liquid ethylenediamine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 34 C (93 F) (closed cup)
  2. Autoignition temperature: 379.4 C (715 F)
  3. Flammable limits in air, % by volume: Lower: 5.8; Upper: 11.1
  4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical
- **Warning properties**
  1. Odor Threshold: The AIHA *Hygienic Guide* states that the ammonia-like odor of ethylenediamine is detectable at 10 ppm.
  2. Eye Irritation Level: Grant notes that "workmen exposed to ethylenediamine are said occasionally to see haloes around objects and to have some blurring of vision, presumably attributable to an effect on the corneal epithelium." Grant does not give any quantitative information, however.

The *Hygienic Guide* reports that ethylenediamine vapor causes eye irritation, but the exact concentrations producing the irritation are not given. They also state that "a chemical cartridge respirator with a cartridge designed for amine vapors may be used for protection against concentrations of ethylenediamine that do not cause eye irritation."

3. Other Information: The *Documentation of TLV's* states that "human subjects found 100 ppm for a few seconds to be inoffensive, but higher concentrations, 200 and 400 ppm, produced noticeable irritation of the nasal mucosa."

4. Evaluation of Warning Properties: Since the odor of ethylenediamine is noticeable at the permissible exposure, this material is treated as a substance 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 ethylenediamine 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 solid or liquid ethylenediamine.
- If employees' clothing has had any possibility of being contaminated with solid ethylenediamine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with solid or liquid ethylenediamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethylenediamine from the clothing. If the

clothing is to be laundered or otherwise cleaned to remove the ethylenediamine, the person performing the operation should be informed of ethylenediamine's hazardous properties.

- Where there is any possibility of exposure of an employee's body to solid or liquid ethylenediamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes wet with liquid ethylenediamine or non-impervious clothing which becomes contaminated with ethylenediamine should be removed immediately and not reworn until the ethylenediamine 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 solid or liquid ethylenediamine or solutions containing ethylenediamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid or solid ethylenediamine or solutions containing more than 5% ethylenediamine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with ethylenediamine should be immediately washed or showered to remove any ethylenediamine.
- Workers subject to skin contact with solid or liquid ethylenediamine should wash any areas of the body which may have contacted ethylenediamine at the end of each work day.
- Eating and smoking should not be permitted in areas where solid or liquid ethylenediamine are handled, processed, or stored.
- Employees who handle solid or liquid ethylenediamine 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 ethylenediamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of carbamate fungicides, pesticides, and weed killers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of chelating agents in dyes, soaps, and cleaning compounds, water treatment, in agriculture, in rubber processing, in pulp and paper processing, and in metal cleaning and electroplating	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of urea resins for use in textile and paper finishing; use in production of textile finishing compounds, resins, rubber products, insecticides, and medicinals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an activator for epoxy resin menders; in preparation of Spandex, adhesives, inks, surface coatings, cross-linking agents, plasticizers, resins curing compounds, and as a dye assist	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of surfactants, emulsifying agents, wetting agents, dispersants, corrosion inhibitors, detergents, and textile surface treatments	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for preparation of dye intermediates, heterocyclic compounds, pharmaceuticals, corrosion inhibitors, adhesives, and salts	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Miscellaneous uses in brightening agent for electroplating, anti-tarnish agent in detergents, lubricant stabilizer, soldering fluxes, processing chemicals for rubber, solvent for casein, albumin, shellac, and sulfur	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 solid or liquid ethylenediamine or solutions containing ethylenediamine 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 solid or liquid ethylenediamine gets on the skin, immediately flush the contaminated skin with water. If solid or liquid ethylenediamine penetrates 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 ethylenediamine, 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 ethylenediamine has 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 or leaks until cleanup has been completed.

• If ethylenediamine 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 liquid form, 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. Ethylenediamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
4. If in the solid form, collect, allow to melt, and dispose of the liquid as above.

• Waste disposal method:

Ethylenediamine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Ethylenediamine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR ETHYLENEDIAMINE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
500 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) providing protection against ethylenediamine. A gas mask with a chin-style or a front- or back-mounted canister providing protection against ethylenediamine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
12000 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 ethylenediamine. 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 ethylenediamine; 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 2000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Ethylene Dibromide *

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_2BrCH_2Br
- Synonyms: 1,2-Dibromoethane; ethylene bromide
- Appearance and odor: Colorless liquid or solid with a mild, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethylene dibromide is 20 parts of ethylene dibromide per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 30 ppm and a maximum peak of 50 ppm for 5 minutes during an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to a ceiling level of 1 mg/m^3 (0.13 ppm) averaged over a 15-minute period. The NIOSH Criteria Document for Ethylene Dibromide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethylene dibromide 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.

- **Effects of overexposure**

1. Short-term Exposure: Ethylene dibromide may cause vomiting, irritation of the eyes, nose, throat, and skin. It may also cause drowsiness. In addition, overexposure may cause damage to the lungs, liver, and kidneys.
2. Long-term Exposure: Prolonged or repeated exposure to ethylene dibromide may cause injury to the lungs, liver, or kidneys. Adverse effects, including abnormalities in offspring, mutations, and stomach cancer, have been found in animals following exposure to ethylene dibromide. The relevance to humans of these findings has not yet been established.
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 ethylene dibromide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethylene dibromide 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 nervous and respiratory systems, heart, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ethylene dibromide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ethylene dibromide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Liver function tests: Ethylene dibromide may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Although ethylene dibromide 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.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where 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.

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—Skin disease: Ethylene dibromide 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.

—Medical warning: Workers should be informed that adverse effects have been found in animals following exposure to ethylene dibromide. These effects have included abnormalities in offspring, mutations, and stomach cancer.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Ethylene dibromide vapor is a narcotic, a severe mucous membrane irritant, and a hepatic toxin. Rats did not survive when exposed to the vapor for longer than 6 minutes at 3000 ppm; minimum lethal concentration for an 8-hour exposure was 200 ppm; these exposures caused hepatic necrosis, pulmonary edema, and cloudy swelling of renal tubules. Four species of animals tolerated daily inhalation of 25 ppm for 6 months without adverse effects but did not tolerate similar exposure to 50 ppm. Accidental use as a human anesthetic resulted in severe irritation of the conjunctiva and respiratory tract, followed by protracted vomiting and death. Excessive exposure may be expected to cause irritation of the eyes and respiratory tract. The liquid is highly irritating to human skin, causing marked erythema and vesiculation. Serious skin injury has been reported from contact with clothing and especially shoes wet with ethylene dibromide. In a bioassay conducted by the National Cancer Institute (NCI), ethylene dibromide was found carcinogenic to rats and mice when fed by gavage. The compound induced squamous cell carcinomas of the fore stomach in rats of both sexes, hepatocellular carcinomas in female rats, and hemangiosarcomas in male rats. In mice of both sexes, the compound induced squamous cell carcinomas of the fore stomach and alveolar/broncheolar adenomas. In NIOSH-sponsored research, laboratory rats exposed to 20 ppm ethylene dibromide by inhalation and also receiving a diet containing 0.05% disulfiram experienced exceedingly high mortality levels as well as a high incidence of tumors (including hemangiosarcomas of the liver, spleen, and kidney).

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 187.9
2. Boiling point (760 mm Hg): 131 C (268 F)
3. Specific gravity (water = 1): 2.18
4. Vapor density (air = 1 at boiling point of ethylene dibromide): 6.5
5. Melting point: 10 C (50 F)
6. Vapor pressure at 20 C (68 F): 11 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.4
8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Heat; ethylene dibromide slowly decomposes in the presence of light.
2. Incompatibilities: Ethylene dibromide reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, magnesium, liquid ammonia, and strong oxidizers.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide, bromine, and carbon monoxide) may be released when ethylene dibromide decomposes.
4. Special precautions: Liquid ethylene dibromide will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

According to the International Labour Office (ILO), the odor of ethylene dibromide is detectable at 10 ppm, well above the NIOSH recommended permissible exposure concentration. Therefore, it is treated as a material with poor warning properties.

Ethylene dibromide is an eye irritant, according to Stecher.

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 ethylene dibromide. 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 Level Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of ethylene dibromide. Each measurement should consist of a 5-minute sample or a series of consecutive samples totalling 5 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 ethylene dibromide 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 ethylene dibromide may be used. An analytical method for ethylene dibromide 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 ethylene dibromide.

• Non-impervious clothing which becomes contaminated with liquid ethylene dibromide should be removed immediately and not reworn until the ethylene dibromide is removed from the clothing.

• Clothing contaminated with liquid ethylene dibromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethylene dibromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethylene dibromide, the person performing the operation should be informed of ethylene dibromide's hazardous properties.

• Where exposure of an employee's body to liquid ethylene dibromide may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Employees should be provided with and required to use splash-proof safety goggles where liquid ethylene dibromide may contact the eyes.

SANITATION

• Skin that becomes contaminated with ethylene dibromide should be immediately washed or showered with soap or mild detergent and water to remove any ethylene dibromide.

• Employees who handle ethylene dibromide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

• Eating and smoking should not be permitted in areas where ethylene dibromide is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethylene dibromide may occur and control methods which may be effective in each case:

Operation	Controls
Use in fumigation operations in preplanting and on grains, fruits, and vegetables	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in production of antiknock fluids and fuels	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in production of water-proofing agents fire extinguishing agents, and gauge fluids during manufacture of measuring intruments	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis in production of dyes, pharmaceuticals, and ethylene oxide; use as a specialty solvent for resins, gums, and waxes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Liberation during production and handling of fumigant preparations	Local exhaust ventilation; general mechanical 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 ethylene dibromide 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 ethylene dibromide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If ethylene dibromide soaks 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 ethylene dibromide, 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 ethylene dibromide 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 ethylene dibromide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. If in the liquid form, collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.
3. If in the solid form, collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing ethylene dibromide should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal methods:

Ethylene dibromide may be disposed of:

1. If in the liquid form, by absorbing it in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill.
2. If in the solid form, by disposing 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 ETHYLENE DIBROMIDE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Vapor Concentration	
400 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.
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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ethylene dibromide; 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 400 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENE DICHLORIDE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about ethylene dichloride 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:** $C_2H_4Cl_2$
- **Structure:** $ClCH_2CH_2Cl$
- **Synonyms:** 1,2-Dichloroethane, dichloroethylene, ethane dichloride, ethylene chloride, glycol dichloride
- **Identifiers:** CAS 107-06-2; RTECS KI0525000; DOT 1184, label required: "Flammable Liquid"
- **Appearance and odor:** Clear, colorless, oily liquid with an odor like chloroform

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.96
2. Boiling point (at 760 mmHg): 83.4°C (182°F)
3. Specific gravity (water = 1): 1.253
4. Vapor density (air = 1 at boiling point of ethylene dichloride): 3.42
5. Melting point: -35.4°C (-31.7°F)
6. Vapor pressure at 20°C (68°F): 68 mm Hg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.81
8. Evaporation rate (butyl acetate = 1): 6.46
9. Saturation concentration in air (approximate) at 25°C (77°F): 11.5% (115,000 ppm)
10. Ionization potential: 11.04 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizers, strong caustics, or chemically active metals such as aluminum or magnesium powder, sodium, or potassium 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 ethylene dichloride.
3. Caution: Ethylene dichloride is corrosive to iron and other metals unless it is stabilizied with alkylamines. Ethylene dichloride will attack some forms of plastics and rubber.

- **Flammability**

1. Flash point: 13°C (55°F) (closed cup)
2. Autoignition temperature: 413°C (775°F)
3. Flammable limits in air, % by volume: Lower, 6.2; Upper, 15.9
4. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 88 ppm
2. Eye irritation levels: 10 ppm
3. 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 ethylene dichloride is 50 parts of ethylene dichloride per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the acceptable ceiling concentration is 100 ppm; and the maximum peak concentration above the acceptable ceiling concentration (maximum duration of 5 minutes in any 3 hours) is 200 ppm. The National Institute for Occupational Safety and Health (NIOSH) recommends that ethylene dichloride 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 [4 milligrams of ethylene dichloride per cubic meter of air (mg/m^3)] as a TWA for up to a 10-hour workshift, 40-hour workweek; the NIOSH ceiling concentration is 2 ppm (8 mg/m^3) as determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 10 ppm

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

(40 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for ethylene dichloride

	Exposure limits ppm	mg/m³
OSHA PEL TWA	50	—
Acceptable ceiling	100	—
Maximum ceiling (5 min in any 3 h)	200	—
NIOSH REL TWA (Ca)*	1	4
Ceiling (15 min)	2	8
ACGIH TLV® TWA	10	40

* (Ca): NIOSH recommends treating as a potential human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

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

• Summary of toxicology

1. *Effects on animals:* Chronic inhalation or ingestion of ethylene dichloride by rats caused pulmonary tissue irritation, congestion, edema and pneumonia, degeneration of liver and kidney tissue, adrenal gland hemorrhage and cell damage, fatty infiltration and hemorrhage of cardiac tissue, and death due to respiratory or cardiac arrest. Cancers of the stomach, circulatory system, mammary glands, uterus, lungs, and skin were produced in similarly exposed rats and mice.

2. *Effects on humans:* Acute inhalation exposure to ethylene dichloride has caused respiratory tract irritation, congestion, edema and pneumonia, impaired functioning of the liver and kidneys, and myocardial hemorrhage. Chronic exposure has produced enlargement and fatty degeneration of the liver, impaired liver and kidney function, depression of nerve conduction, anemia, and increased serum bile salt levels. Ethylene dichloride has been detected in the milk of exposed lactating mothers.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to ethylene dichloride can cause headache, weakness, pain or irritation of the eyes and skin, bluish discoloration of skin and mucous membranes (cyanosis), nausea, vomiting, mental confusion, dizziness, incoordination, and unconsciousness.

2. *Long-term (chronic):* Exposure to ethylene dichloride can cause headache, fatigue, irritability, nervousness, cough, weakness, diarrhea, and muscle tremor. Severe irritation of the skin, edema, and tissue destruction (necrosis) 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 ethylene dichloride, 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 reproductive, 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 ethylene dichloride 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 ethylene dichloride. 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 eyes, skin, liver, kidneys, and reproductive, cardiovascular, 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. Because occupational exposure to ethylene dichloride 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: None recognized (however, toxic hepatitis is a recognized SHE associated with occupational exposure to ethylene dibromide).

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to ethylene dichloride 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 ethylene dichloride. 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 for ethylene dichloride may be performed by collecting ethylene dichloride vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure ethylene dichloride may also be used if available. A detailed sampling and analytical method for ethylene dichloride 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, and other appropriate protective clothing necessary to prevent skin contact with ethylene dichloride.

SANITATION

Clothing which is contaminated with ethylene dichloride 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 ethylene dichloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethylene dichloride'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 ethylene dichloride 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 ethylene dichloride 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 ethylene dichloride 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 ethylene dichloride

Operations	Controls
During use as a chemical intermediate in the manufacture of vinyl chloride	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an intermediate in the production of chlorinated solvents and ethyleneamines	Process enclosure, local exhaust ventilation, personal protective equipment
During the production of gasoline using tetraethyl lead as an anti-knock agent and ethylene dichloride as a lead scavenger	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a fumigant or industrial solvent	Local exhaust ventilation, personal protective equipment
During the manufacture of ethylene dichloride	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 ethylene dichloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethylene dichloride 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 ethylene dichloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethylene dichloride gets on the skin, wash it immediately with soap and water. If ethylene dichloride 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 ethylene dichloride 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 ethylene dichloride, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing ethylene dichloride may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing ethylene dichloride 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 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 Enforce-

ment 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 ethylene dichloride

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 ETHYLENE GLYCOL

INTRODUCTION

This guideline summarizes pertinent information about ethylene glycol 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**

  $C_2H_6O_2$

- **Structure**

  CH_2OHCH_2OH

- **Synonyms**

  1,2-Dihydroxyethane; 1,2-ethanediol; 2-hydroxyethanol; ethane-1,2-diol; ethylene alcohol; ethylene dihydrate; glycol; monoethylene glycol; glycol alcohol; Lutrol-9; Macrogol 400BPC; Norkool; Dowtherm SR 1

- **Identifiers**

  1. CAS No.: 107-21-1
  2. RTECS No.: KW2975000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Ethylene glycol is a combustible, slightly viscous, colorless liquid with a sweet taste and no odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 62.1
  2. Boiling point (760 mm Hg): 197.6°C (387.7°F)
  3. Specific gravity (water = 1): 1.11 at 20°C (68°F)
  4. Vapor density: 2.1
  5. Melting/freezing point: -13°C (8.6°F)
  6. Vapor pressure at 20°C (68°F): 0.06 mm Hg
  7. Solubility: Miscible in water, ethanol, glycerol, acetic acid, and acetone; slightly soluble in ether; practically insoluble in benzene and its homologs, chlorinated hydrocarbons, petroleum ether, and oils.
  8. Evaporation rate: Data not available

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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

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame. Ethylene glycol that is heated or misted into the air presents a moderate fire and explosion hazard.

2. Incompatibilities: Ethylene glycol can react dangerously with chlorosulfonic acid, oleum, sulfuric acid, and strong oxidizing agents such as perchlorates, peroxides, permanganates, chlorates, and nitrates.

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

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 1 (slight fire hazard) to ethylene glycol.

1. Flash point: 115°C (240°F) (open cup); 111°C (232°F) (closed cup)

2. Autoignition temperature: 398°C (748°F)

3. Flammable limits in air (percent by volume): Lower, 3.2; upper, data not available

4. Extinguishant: Use water spray, dry chemical, "alcohol" foam, or carbon dioxide to fight fires involving ethylene glycol. Water or foam may cause frothing. 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 dilute spills to noncombustible mixtures.

Fires involving ethylene glycol 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 ethylene glycol 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 is 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 a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving ethylene glycol. Structural firefighters' protective clothing may provide limited protection against fires involving ethylene glycol.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethylene glycol [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 ethylene glycol [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) assigns ethylene glycol a ceiling limit value of 50 ppm (127 mg/m^3), which should not be exceeded during any part of the working exposure [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of respiratory tract irritation associated with exposure to ethylene glycol [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to airborne concentrations of ethylene glycol causes eye and upper respi-

ratory tract irritation, and ingestion causes central nervous system depression, kidney and liver injury, and fetotoxic and developmental effects in experimental animals. In contact with the eyes or skin of rabbits, ethylene glycol caused irritation classified as mild [NIOSH 1994]. The dermal LD_{50} in rabbits is 9,530 mg/kg [NIOSH 1994]. The oral LD_{50} is 4,700 mg/kg in rats, 5,500 mg/kg in mice, and 6,610 mg/kg in guinea pigs [NIOSH 1994]. Dogs and cats given oral doses of ethylene glycol developed ataxia, vomiting, polydipsia, and seizures before losing consciousness [NLM 1993]. Exposure to a 12-mg/m^3 concentration of ethylene glycol continuously for 90 days, however, caused a moderate to severe degree of eye irritation in rabbits and rats [ACGIH 1991]. Dietary levels of ethylene glycol as high as 2 percent for 2 years caused decreased life span, calcium oxalate bladder stones, and kidney and liver damage in rats; the no-effect level in this study was no more than 0.2 percent in the diet (100 mg/kg/day) for 2 years [Clayton and Clayton 1981]. Several studies in rats and mice given oral doses of ethylene glycol during pregnancy have shown fetotoxic and developmental effects [NIOSH 1994].

2. *Effects on Humans:* Exposure to ethylene glycol vapor or mist causes eye, nose, and upper respiratory tract irritation in humans. In one report, reversible conjunctival inflammation occurred after ethylene glycol was splashed into a worker's eye [Hathaway et al. 1991]. By ingestion or percutaneous absorption, ethylene glycol causes central nervous system effects, liver and kidney damage, and cardiopulmonary effects. Loss of consciousness and nystagmus were reported among 9 of 38 women exposed to ethylene glycol vapor, and 5 of these workers also showed lymphocytosis [Clayton and Clayton 1981]. Throat irritation, headache, and backache were reported in human volunteers exposed to a mean concentration of ethylene glycol mist ranging from 1.4 to 27 ppm for 20 to 22 hours/day for 4 weeks. At a concentration of 60 ppm, symptoms were common; at 80 ppm, coughing and a sensation of tracheal burning became intolerable [ACGIH 1991]. Ingestion of a large amount (100 ml or more) of ethylene glycol produces three well-documented stages of toxicity. In Stage 1, which occurs within 30 minutes, nausea and vomiting, slurred speech, ataxia, nystagmus, lethargy, and a faint, sweetish odor on the breath develop. Coma, convulsions, and respiratory depression or cardiovascular collapse also may occur at this stage. In Stage 2, cardiopulmonary effects progress and cyanosis, pulmonary edema, and congestive heart failure may develop. In Stage 3, acute tubular necrosis develops, with oxaluria or anuria; these signs may progress to uremia and renal failure [Clayton and Clayton 1981; Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute airborne exposure to ethylene glycol include redness and irritation of the eyes and eyelids, sore throat, runny nose, cough, headache, and backache. Massive ingestion causes nausea; vomiting; slurred speech; ataxia; nystagmus; lethargy; impaired vision; a faint, sweet odor on the breath; coma; convulsions; elevated body temperature; elevated heart and respiratory rates; hypotension; agitation; confusion; cyanosis; tremor; areflexia; muscle twitches or contractions; crystalluria; hematuria; proteinuria; oxaluria; anuria; uremia; and cardiopulmonary collapse.

2. *Chronic exposure:* No signs or symptoms of chronic exposure to ethylene glycol have been reported in humans.

- **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 ethylene glycol. ***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 car-

diopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if ethylene glycol 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, 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 ethylene glycol and lead to worker exposures to this substance:

—Use as antifreeze in cooling and heating systems

—Use as a vehicle for pharmaceutical preparations, food extracts, and flavoring essences and as a component of skin lotions, a substitute for glycerin, and an ingredient in various powders

—Use in electrolytic condensers as a solvent for boric acid and borates

—Use as a solvent in the paint and plastics industries

—Use in the formulation of printers' inks, stamp pad inks, and inks for ball point pens

—Use in the synthesis of safety explosives, glyoxal, unsaturated ester-type alkylated resins, plasticizers, elastomers, synthetic fibers (terylene and dacron), and synthetic waxes

—Use as an industrial humectant

The following methods are effective in controlling worker exposures to ethylene glycol, 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.

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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 ethylene glycol, 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, upper 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 ethylene glycol 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, upper 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 ethylene glycol exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethylene glycol on the eyes, upper 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. Although several of the metabolites of ethylene glycol can be detected in body fluids (serum, urine, blood) of exposed individuals, levels of these metabolites do not correlate well with airborne concentrations of ethylene glycol. Therefore, no biological monitoring test acceptable for routine use has yet been developed for ethylene glycol.

- **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 ethylene glycol is made using a glass fiber filter in a Swinnex (TM) cassette, followed by a silica gel tube (520/260 mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a minimum collection time of 5 minutes is reached. As soon as possible after sampling, the filter is removed from the cassette and placed in a vial with a Teflon-lined cap containing 1 mL of 2% isopropanol in water. Analysis is conducted by gas chromatography using a flame ionization detector. This method is described in the OSHA Computerized Information System [OSHA 1993] and in Method No. 5500 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If ethylene glycol contacts the skin, workers should flush the affected areas with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with ethylene glycol 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 ethylene glycol, particularly its potential to be irritating to the eyes, nose, and upper respiratory tract.

A worker who handles ethylene glycol 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 ethylene glycol or a solution containing ethylene glycol is handled, processed, or stored.

STORAGE

Ethylene glycol 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]. Since some containers can affect the color of this material, resin-coated steel, glass, aluminum, or stainless steel containers should be used for storage. Containers of ethylene glycol should be protected from physical damage and should be stored separately from chlorosulfonic or sulfuric acid, oxidizing agents such as perchlorates, peroxides, permanganates, chlorates, nitrates, moisture, heat, sparks, and open flame. Because containers that formerly contained ethylene glycol may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethylene glycol, 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, but the spray may not prevent ignition in closed spaces.

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 ethylene glycol 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**

  Ethylene glycol 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 ethylene glycol; 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 who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of ethylene glycol 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 ethylene glycol 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 ethylene glycol 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 ethylene glycol 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 ethylene glycol. 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 ethylene glycol and have demonstrated good-to-excellent resistance for periods of greater than 8 hr: natural rubber, butyl rubber, neoprene, polyvinyl chloride, nitrile rubber, polyethylene, Teflon, Viton, Saranex, and Barricade. 4H and Responder have demonstrated good-to-excellent resistance for periods of greater than 4 hr and less than 8 hr. Polyvinyl alcohol has a breakthrough time of 1 to 4 hr and should be used with caution against ethylene glycol.

If ethylene glycol 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 ethylene glycol 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 ethylene glycol. Contact lenses should not be worn if the potential exists for ethylene glycol exposure.

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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.

NIOSH [1994]. Registry of toxic effects of chemical substances database: ethylene glycol. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

NLM [1992]. The hazardous substances data bank: ethylene glycol. Bethesda, MD: National Library of Medicine.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR NITROGLYCERIN AND ETHYLENE GLYCOL DINITRATE

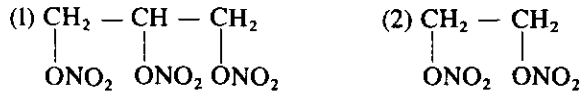
INTRODUCTION

This guideline summarizes pertinent information about nitroglycerin (NG) and ethylene glycol dinitrate (EGDN) 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 (1) nitroglycerin and (2) ethylene glycol dinitrate.

- **Formula:** (1) $C_3H_5N_3O_9$ (2) $C_2H_4N_2O_6$
- **Structure:**



- **Synonyms:** (1) Anginine, blasting gelatin, blasting oil, glonoin, glycerol trinitrate, glyceryl nitrate, glyceryl trinitrate, GTN, myocon, NG, niglycon, niong, nitric acid triester of glycerol, nitrine-TDC, nitroglycerol, nitroglyn, nitrol; (2) Dinitroglycol, EGDN, ethanediol dinitrate, ethylene dinitrate, ethylene nitrate, glycol dinitrate, nitroglycol
- **Identifiers:** (1) CAS 55-63-0; RTECS QX2100000; DOT not assigned; (2) CAS 628-96-6; RTECS KW5600000; DOT not assigned
- **Appearance and odor:** (1) Pale yellow, slightly sweet smelling oil; (2) yellowish liquid with no odor

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for (1) nitroglycerin and (2) ethylene glycol dinitrate. If not specified, data apply to both compounds.

- **Physical data**

1. Molecular weight: (1) 227.11; (2) 152.08
2. Boiling point (at 760 mmHg): (1) 256°C (493°F); (2) 197-200°C (387-392°F)
3. Explosive point: (1) 270°C (518°F); (2) 114°C (237°F)
4. Specific gravity (water = 1): (1) 1.6; (2) 1.49
5. Vapor density: (1) 7.8 (air = 1 at boiling point of NG); (2) 5.24 (air = 1 at boiling point of EGDN)
6. Melting point: (1) 13.1°C (55.1°F); (2) -22.3°C (-9°F)
7. Vapor pressure at 20°C (68°F): (1) 0.00012-0.011 mmHg; (2) 0.04 mmHg
8. (1) Slightly soluble in water; (2) insoluble in water

- **Reactivity**

1. Incompatibilities: Contact with acids, heat, or mechanical shock may result in explosion.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in an explosion involving NG or EGDN.

- **Flammability**

1. Flash point: Explodes
2. Autoignition temperature: (1) 270.4°C (518°F); (2) 195°C (383°F)
3. Class A Explosive (29 CFR 1910.109), Flammability Rating 2 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, NG and EGDN should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for NG and EGDN is 0.2 parts of NG or EGDN per million parts of air (ppm) [2 milligrams of NG or 1 milligram of EGDN per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded (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) recommended exposure limit (REL) for NG or EGDN alone or for mixtures of the two substances is 0.1 mg/m^3 as a ceiling concentration determined in any 20-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for NG or EGDN is

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0.05 ppm (0.5 mg/m³ NG or 0.3 mg/m³ EGDN) as a time-weighted average concentration (TWA) for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational exposure limits for nitroglycerin and ethylene glycol dinitrate

	Exposure limits ppm	mg/m³
OSHA PEL		
NG ceiling (Skin)*	0.2	2
EGDN ceiling (Skin)†	0.2	1
NIOSH REL		
Ceiling (20 min)	—	0.1
ACGIH TLV®		
NG TWA (Skin)	0.05	0.5
EGDN TWA (Skin)	0.05	0.3

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† If the atmospheric concentration of EGDN exceeds 0.02 ppm, personal protection may be necessary to avoid headache.

HEALTH HAZARD INFORMATION

• Routes of exposure

NG and EGDN may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• Summary of toxicology

1. *Effects on animals:* Subchronic inhalation of EGDN by mice caused lethargy, skin damage, muscle spasms, and death due to circulatory and respiratory paralysis. In cats, subchronic or chronic inhalation or dermal administration of EGDN caused severe anemia, decreased appetite, seizures, hemorrhage of internal organs, and death. Chronic oral administration of NG to rats produced cancer of the liver. NIOSH will continue to monitor the research regarding NG to determine whether the collective evidence justifies controlling this chemical as a carcinogen.

2. *Effects on humans:* Acute inhalation or dermal exposure of workers to NG and EGDN has caused decreased systolic, diastolic, and pulse blood pressures due to vascular dilation. Chronic exposure to NG and EGDN has caused damage to the heart and reduced tolerance to alcohol. Chronic exposure to NG and EGDN, or to NG alone, followed by a brief or extended period away from exposure, has been associated with an increased incidence of sudden death.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to NG and EGDN can cause severe headache, dizziness, nausea, and heart palpitations.

2. *Long-term (chronic):* Exposure to NG and EGDN can cause severe chest pain (angina pectoris), which frequently occurs during brief periods away from work. Skin sensitization 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 NG or EGDN, 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 nervous, cardiovascular, and hematopoietic (blood-cell-forming) 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 NG or EGDN 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 disease, especially coronary artery 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 NG or EGDN. 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 nervous, hematopoietic, and cardiovascular sys-

tems 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 NG or EGDN may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include methemoglobinemia.
2. Delayed-onset SHE's include methemoglobinemia and chest pain (angina pectoris).

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of NG and EGDN. 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 20-minute sample or a series of consecutive samples that total 20 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 NG and EGDN vapors with tenax solid sorbent tubes followed by desorption with ethanol and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure NG and EGDN may also be used if available. A detailed sampling and analytical method for NG and EGDN may be found in the *NIOSH Manual of Analytical Methods* (method number 2507).

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 NG and EGDN.

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

SANITATION

Clothing which is contaminated with NG or EGDN 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 NG and EGDN from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of NG and EGDN's hazardous properties.

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

Skin that becomes contaminated with NG or EGDN 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 NG or EGDN 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 NG and EGDN 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 nitroglycerin and ethylene glycol dinitrate

Operations	Controls
During formulation and filling operations in the manufacture of industrial explosives and propellants	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the synthesis and handling of NG or EGDN; during the handling of industrial explosives	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the preparation and handling of dosage forms including tablets and solutions in the manufacture of pharmaceuticals	Process enclosure, 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 NG or EGDN, an eye-wash fountain should be provided within the immediate work area for emergency use.

If NG or EGDN 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 these compounds.

• **Skin exposure**
Where there is any possibility of a worker's body being exposed to NG or EGDN, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If NG or EGDN gets on the skin, wash it immediately with soap and water. If NG or EGDN 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 NG or EGDN 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 NG or EGDN, absorb on sponges or paper towels kept in a sodium carbonate solution. Remove paper towels to a secure outdoor location for burning.
4. Large quantities of liquids containing NG or EGDN may be washed with water into holding tanks where NG and EGDN can be separated. NG and EGDN should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in solid form, NG and EGDN may be collected using nonsparking tools and removed to a secure, outdoor location for burning.

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 nitroglycerin and ethylene glycol dinitrate

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.2 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)
Less than or equal to 0.5 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 2 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 20 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 40 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 40 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 0.1 mg/m^3 (ceiling).

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLENEIMINE

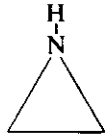
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about ethyleneimine 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_5N
- **Structure:**



- **Synonyms:** Aminoethylene, azirane, dihydroazirene, dihydro-lh-azirine, dimethyleneimine, dimethylenimine
- **Identifiers:** CAS 151-56-4; RTECS KX5075000; DOT 1185, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Colorless volatile liquid with an intense odor like ammonia

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 43.08
2. Boiling point (at 760 mmHg): 56°C (132°F)
3. Specific gravity (water = 1): 0.8321
4. Vapor density (air = 1 at boiling point of ethyleneimine): 1.5
5. Melting point: -59°C (-74°F)
6. Vapor pressure at 20°C (68°F): 160 mmHg
7. Soluble in water

- **Reactivity**

1. Incompatibilities: Contact with silver, aluminum, or acid may cause explosive polymerization.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving ethyleneimine.

- **Flammability**

1. Flash point: -11.1°C (12°F) (closed cup)
2. Autoignition temperature: 320°C (608°F)
3. Flammable limits in air, % by volume: Lower, 3.6; Upper, 46
4. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 2 ppm
2. Eye irritation levels: 100 ppm
3. 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) permissible exposure limit (PEL) for ethyleneimine is 0.5 ppm [1.0 milligram of ethyleneimine per cubic meter of air (mg/m^3)] (Skin) as a time-weighted average (TWA) concentration over an 8-hour workshift. The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The OSHA standard requires implementation of stringent controls wherever ethyleneimine or solid or liquid mixtures containing at least 0.1% by weight or volume of ethyleneimine 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 1910.1012, Ethyleneimine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (1.0 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

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• **Summary of toxicology**

1. *Effects on animals:* In rabbits and cats, acute instillation of ethyleneimine in the eyes caused damage, blindness, and death; oral administration of ethyleneimine to rats caused decreased white blood cell counts and tissue degeneration of the liver, kidneys, and heart. Subchronic subcutaneous injection of ethyleneimine in rats produced injection-site skin cancer. Chronic oral administration of ethyleneimine to mice produced cancers of the liver and lungs.

2. *Effects on humans:* Acute inhalation or dermal exposure of laboratory workers has caused central nervous system (CNS) effects, excess fluid in the lungs, damage to the liver and kidneys, and in some cases, death.

• **Signs and symptoms of exposure**

Short-term exposure (acute): Exposure to ethyleneimine can cause delayed onset headache, dizziness, nausea, and vomiting. Skin sensitization and severe irritation and inflammation of the eyes, nose, and throat 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 ethyleneimine, 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 ethyleneimine 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 diseases of the liver or skin or concurrent dermatitis. The physician should obtain baseline values for tests of liver function.

• **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 ethyleneimine. 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 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 ethyleneimine 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

• **Method**

Sampling and analysis may be performed by collecting ethyleneimine vapors with bubblers containing Folin's reagent followed by extraction with chloroform and analysis by high-pressure liquid chromatography. Direct-reading devices calibrated to measure ethyleneimine may also be used if available. A detailed sampling and analytical method for ethyleneimine may be found in the *NIOSH Manual of Analytical Methods* (method number 300).

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 ethyleneimine 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 ethyleneimine 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 ethyleneimine 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 ethyleneimine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethyleneimine'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 ethyleneimine 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 1910.1012:

Areas where ethyleneimine 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 are 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 ethyleneimine, local and systemic toxicity, the specific nature of the operations 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 ethyleneimine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of ethyleneimine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where ethyleneimine 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 ethyleneimine 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 ethyleneimine from materials, equipment, and the decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to ethyleneimine 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 ethyleneimine

Operations	Controls
During use in the manufacture of paper, textiles, adhesives, binders, petroleum refining products, rocket and jet fuels, lubricants, chemo-sterilant chemicals, chemotherapeutic agents, coating resins, varnishes, lacquers, agricultural chemicals, cosmetics, ion-exchange resins, photographic chemicals, colloid flocculants, and surfactants	Process enclosure, restricted access, local exhaust ventilation where appropriate, 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 ethyleneimine, 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 ethyleneimine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethyleneimine 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 ethyleneimine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethyleneimine gets on the skin, wash it immediately with soap and water. If ethyleneimine 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 ethyleneimine 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 ethyleneimine, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing ethyleneimine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing ethyleneimine may be collected by vacuuming with an appropriate system. If a vacuum system is used to remove ethyleneimine, 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 ethyleneimine

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 ETHYLENE OXIDE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about ethylene oxide 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_4O

• **Structure:**

• **Synonyms:** Anprolene; dihydrooxirene; dimethylene oxide; EO; 1,2-epoxyethane; EtO; oxacyclopropane; oxane; oxiran; oxirane

• **Identifiers:** CAS 75-21-8; RTECS KX2450000; DOT 1040, label required: "Flammable Liquid"

• **Appearance and odor:** Colorless liquid or gas with an etherlike odor

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 44.06
2. Boiling point (at 760 mmHg): 10.7°C (51.3°F)
3. Specific gravity (water = 1): 0.8711
4. Vapor density (air = 1 at boiling point of ethylene oxide): 1.5
5. Melting point: -111.3°C (-168°F)
6. Vapor pressure at 20°C (68°F): 1,095 mmHg
7. Soluble in water
8. Ionization potential: 10.56 eV

• **Reactivity**

1. Incompatibilities: Ethylene oxide reacts readily with alkali metal hydroxides or highly active catalysts (e.g., anhydrous chlorides of iron, tin, or aluminum and oxides of iron or aluminum); ethylene oxide should not come in contact with copper.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving ethylene oxide.
3. Caution: Protect container against physical damage. Store in an outside area in insulated tanks or containers shielded from sun and heat. Ethylene oxide may interact with some plastics, coatings, and rubber.

• **Flammability**

1. Flash point: -6°C (20°F) (open cup)
2. Autoignition temperature: 429°C (804°F)
3. Flammable limits in air, % by volume: Lower, 3; Upper, 100
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or water spray or fog
5. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)
6. All ignition sources, including static electricity, should be controlled. Flashback along a vapor trail may occur.

• **Warning properties**

1. Odor threshold: 430 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 ethylene oxide is 1 part of ethylene oxide per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommends that ethylene oxide 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 5 ppm [9 milligrams per cubic meter (9 mg/m³)] as a ceiling concentration determined in any 10-minute sampling period and not to be achieved for more than 10 minutes dur-

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

ing any workday. In addition, NIOSH recommends that exposure to ethylene oxide be less than 0.1 ppm (0.18 mg/m³) as a TWA for up to an 8-hour workshift, 40-hour workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated ethylene oxide as an A2 substance (suspected of carcinogenic potential for man) having an assigned threshold limit value (TLV®) of 1 ppm (2 mg/m³) as a TWA for a normal 8-hour workday and 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for ethylene oxide

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	1	—
NIOSH REL TWA		
(Ca)*	<0.1	<0.18
Ceiling (10 min/day)	5	9
ACGIH TLV® TWA		
(A2)†	1	2

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected of carcinogenic potential for man.

HEALTH HAZARD INFORMATION

• Routes of exposure
Ethylene oxide 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 ethylene oxide by rats and guinea pigs caused pulmonary edema, paralysis, and corneal opacities. Subchronic inhalation of ethylene oxide by male and female rats prior to mating and during pregnancy caused a decrease in the number of pregnant females and in the number of offspring per litter. Chronic oral administration of ethylene oxide to rats produced cancer of the forestomach; chronic inhalation produced brain tumors, leukemia, and cancer of the peritoneum.
2. *Effects on humans:* Chronic exposure to ethylene oxide has caused anemia, peripheral neuropathy, and chromosomal damage in white blood cells (lymphocytes). Exposure to ethylene oxide has been associated with increased incidences of miscarriage, leukemia, and stomach cancer.

• Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to ethylene oxide can cause nausea, headache, weakness, vomiting, drowsiness, incoordination, and irritation of the eyes, nose, throat, and lungs. Skin contact with ethylene oxide can cause blisters, edema, burns, frostbite, and severe dermatitis.
2. *Long-term (chronic):* Exposure to ethylene oxide can cause skin sensitization, numbing of the sense of smell, and respiratory infection.

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 ethylene oxide, 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, gastrointestinal tract, and hematopoietic (blood cell forming), nervous, 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 ethylene oxide 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. In addition to the medical interview and physical examination, the physician should consider obtaining additional baseline electrophysiologic and electromyographic studies and an assess-

ment of fertility, using standardized methods and evaluation criteria.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinatons may be necessary should a worker develop symptoms that may be attributed to exposure to ethylene oxide. The interviews, examinations, and appropriate medical screening and/or biologic monitoring test should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the eyes, skin, gastrointestinal tract, and hematopoietic, nervous, 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 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 ethylene oxide 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 ethylene oxide 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 ethylene oxide. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 10-minute sample or a series of consecutive samples that total 10 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 ethylene oxide 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 ethylene oxide may be used if available. A detailed sampling and analytical method for ethylene oxide may be found in the *NIOSH Manual of Analytical Methods* (method number 1607).

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 liquid ethylene oxide.

SANITATION

Clothing which is contaminated with liquid ethylene oxide 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 ethylene oxide from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethylene oxide'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 ethylene oxide 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 ethylene oxide 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 ethylene oxide 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 ethylene oxide

Operations	Controls
During synthesis and handling of ethylene oxide	Process enclosure, local exhaust ventilation, personal protective equipment
During synthesis of ethylene glycols, glycol ethers, ethanolamines, amines, nonionic surface-active agents	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a sterilizing agent	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 ethylene oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethylene oxide 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 liquid ethylene oxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethylene oxide gets on the skin, wash it immediately with soap and water. If liquid ethylene oxide 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 ethylene oxide is spilled or leaked, the following steps should be taken:

1. If ethylene oxide is in the gaseous form, stop the flow of 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. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing ethylene oxide, 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 duct work is free from ethylene oxide vapors. Burn the paper in a suitable location away from combustible materials.
5. Large quantities of liquids containing ethylene oxide may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Ethylene oxide should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
6. Liquids containing ethylene oxide 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

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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 ethylene oxide

Condition	Minimum respiratory protection*†
Concentration:	
Less than 5 ppm	Any air-purifying, full-facepiece canister respirator that provides protection against ethylene oxide and is equipped with an effective end-of-service-life indicator (ESLI)
	Any self-contained breathing apparatus equipped with a full facepiece
	Any supplied-air respirator with a full facepiece
Equal to or greater than 5 ppm, or planned or emergency entry into environments containing unknown concentrations	Any self-contained breathing apparatus equipped with a full facepiece and operated in a pressure-demand or positive-pressure mode
	Any supplied-air respirator equipped 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 equipped with a full facepiece and operated in a pressure-demand or other positive-pressure mode
Escape only	Any air-purifying, full-facepiece canister respirator that provides protection against ethylene oxide and is equipped with an effective ESLI
	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 <0.1 ppm (<0.18 mg/m³) (TWA).

Occupational Health Guideline for Ethyl Ether

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: $C_2H_5OC_2H_5$
- Synonyms: Diethyl ether; ethyl oxide; ether; diethyl oxide; sulfuric ether
- Appearance and odor: Colorless liquid with a characteristic, sweet ether odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl ether is 400 parts of ethyl ether per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1200 milligrams of ethyl ether per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl ether 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 ethyl ether may cause irritation of the eyes, nose, and throat. It may also cause dizziness, drowsiness, unconsciousness, and death.

2. Long-term Exposure: Prolonged overexposure may cause loss of appetite, dizziness, drowsiness, headache, exhaustion, excitation, and mental disturbances. It may also increase the severity of the effects of drinking alcoholic beverages. Repeated exposure may be habit forming.

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 ethyl ether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl ether 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 ethyl ether exposure.

—Skin disease: Ethyl ether 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 ethyl ether 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 ethyl ether 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 ethyl ether 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**

Ethyl ether has predominantly narcotic properties leading to anesthesia; it is also an eye and respiratory irritant. Continued inhalation of 2000 ppm in human subjects may produce dizziness. Higher concentrations produce vomiting, pallor, and irregular respiration. Temporary aftereffects are salivation, vomiting, respi-

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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ratory tract irritation, headache, and either depression or excitation. Chronic exposure results in some persons in anorexia, exhaustion, headache, drowsiness, dizziness, excitation, and psychic disturbances. Albuminuria has been reported. Tolerance may be acquired through repeated exposures. Ethyl ether is a mild skin irritant; repeated exposure causes drying and cracking. The vapor is irritating to the eye, and the undiluted liquid causes painful inflammation of a transitory nature. Human subjects found 200 ppm irritating to the nose, but not to the eyes or throat. Permanent aftereffects are rare.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.1
2. Boiling point (760 mm Hg): 35 C (95 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of ethyl ether): 2.6
5. Melting point: −123 C (−190 F)
6. Vapor pressure at 20 C (68 F): 442 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 7.5
8. Evaporation rate (butyl acetate = 1): 37.5

- **Reactivity**

1. Conditions contributing to instability: Heat; sunlight
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 ethyl ether.
4. Special precautions: Ethyl ether will attack some forms of plastics, rubber, and coatings. Ethers, which have been in contact with air or exposed to light for a long time, may contain peroxides. Ethers which contain peroxides may explode when the caps or stoppers of their containers are removed. Ethyl ether, being a nonconductor, may accumulate static electric charges that may result in ignition of its vapors.

- **Flammability**

1. Flash point: −45 C (−49 F) (closed cup)
2. Autoignition temperature: 160 C (320 F)
3. Flammable limits in air, % by volume: Lower: 1.9; Upper: 36.0
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for ethyl ether of 0.33 ppm. Patty notes that the odor is pungent.
2. Eye Irritation Level: Grant states that ethyl ether "causes a transitory smarting sensation if splashed in the eye or if a high vapor concentration contacts the eye, but momentary exposure generally does not cause injury. Prolonged exposure of the cornea to high concentration of ether vapor, such as employed in general anesthesia, does cause superficial epithelial injury, from which recovery is usually prompt." Patty also reports that in high concentrations ethyl ether causes eye irritation.
3. Other Information: Patty reports that "Nelson et al. reported that human subjects found ethyl ether irritating to the nose, but not to the eyes or throat, at a vapor concentration of 200 ppm."
4. Evaluation of Warning Properties: Through its odor and nasal irritation, ethyl ether can be detected below 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 ethyl ether vapors using an adsorption tube with subsequent desorption with ethyl acetate and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl ether may be used. An analytical method for ethyl ether 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 ethyl ether.
- Clothing wet with liquid ethyl ether should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl ether from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl ether, the person performing the operation should be informed of ethyl ether's hazardous properties.
- Any clothing which becomes wet with liquid ethyl ether should be removed immediately and not reworn until the ethyl ether is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl ether may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl ether may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in manufacture of smokeless powder	Local exhaust ventilation; general dilution ventilation
Use as a laboratory solvent and chemical extractant	General dilution ventilation; personal protective equipment
Use as a solvent cleaning agent in shoe and textile industries	General dilution ventilation; personal protective equipment
Use as an anesthetic	General dilution ventilation
Liberation from manufacture of alkali or sodium ethylxanthotes by heated processes; from manufacture of warm-process pharmaceuticals; from manufacture of chemicals from cold processes – Grignard reactions and acetic acid recovery	Process enclosure; general dilution ventilation; local exhaust ventilation
Use as a solvent in manufacture of textiles, cellulose acetate, plastics, and dyes	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during manufacture of cold-process pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as an additive in motor fuels, perfumes, and denatured alcohol	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in the priming of gasoline engines in cold climates	General dilution ventilation
Liberation during refueling of diesel engines in cold climates	General dilution ventilation
Use as an anesthetic by animal handlers	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 ethyl ether 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 ethyl ether gets on the skin, promptly wash the contaminated skin with water if the ethyl ether has not already evaporated. If ethyl ether soaks 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 ethyl ether, 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 ethyl ether 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 ethyl 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, 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, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Ethyl ether should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Ethyl ether may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol, and by atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR ETHYL ETHER

Condition	Minimum Respiratory Protection* Required Above 400 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
4000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
19,000 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 19,000 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 Ethyl Formate

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: $HCOOC_2H_5$
- Synonyms: Ethyl methanoate; formic acid ethyl ester
- Appearance and odor: Colorless liquid with a fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl formate is 100 parts of ethyl formate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 300 milligrams of ethyl formate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl formate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ethyl formate may cause irritation of the eyes, nose, throat. and skin. At high concentrations it may cause drowsiness and unconsciousness.

2. Long-term Exposure: Long-term overexposure to ethyl formate 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 ethyl formate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl formate 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 ethyl formate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl formate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: This substance 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 ethyl formate 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 ethyl formate 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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Ethyl formate is irritating to the eyes and nose at concentrations of 330 ppm. Narcosis occurs in animals, but only at exposure levels near the lethal concentration of 10,000 ppm. Dogs exposed to this very high concentration died of pulmonary edema. Rats survived at 4000 ppm. Application to the skin caused only slight irritation; when dropped into the eye, it caused moderate injury to the cornea. 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.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74
2. Boiling point (760 mm Hg): 54.5 C (130 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of ethyl formate): 2.6
5. Melting point: −79 C (−110 F)
6. Vapor pressure at 20 C (68 F): 194 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 13.6
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
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 ethyl formate.
4. Special precautions: None

- **Flammability**

1. Flash point: −20 C (−4 F) (closed cup)
2. Autoignition temperature: 455 C (851 F)
3. Flammable limits in air, % by volume: Lower: 2.8; Upper: 16
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No information is available concerning the odor threshold of ethyl formate.
2. Eye Irritation Level: According to the *Documentation of TLV's*, "in man, a concentration of 330 ppm produced a slight irritation of the eyes and a rapidly increasing nasal irritation . . . . A threshold limit of 100 ppm is recommended to prevent eye and nasal irritation."
3. Evaluation of Warning Properties: Since eye and nasal irritation occur at a concentration which is approximately only three times the permissible exposure limit, ethyl formate 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 ethyl formate 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 ethyl formate may be used. An analytical method for ethyl formate 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 ethyl formate.
- Any clothing which becomes wet with liquid ethyl formate should be removed immediately and not reworn until the ethyl formate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl formate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid ethyl formate should be promptly washed or showered to remove any ethyl formate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl formate may occur and control methods which may be effective in each case:

Operation	Controls
Use during spray, brush, or dip applications of lacquers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for cellulose acetate in artificial silk manufacture	General dilution ventilation; personal protective equipment
Use in shoe industry to dissolve celluloid heel coverings; use as a solvent in manufacture of artificial leather	General dilution ventilation; personal protective equipment
Use in manufacture of safety glass	General dilution ventilation
Use as a fumigant and larvacide for tobacco, cereals, and dried fruits	Personal protective equipment
Liberation during use as an intermediate in organic synthesis	General dilution ventilation
Liberation during formulation of synthetic flavors	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 ethyl formate 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 ethyl formate gets on the skin, immediately flush the contaminated skin with water. If ethyl formate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of ethyl formate, 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 ethyl formate 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 ethyl formate 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. Ethyl formate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Ethyl formate 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.

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RESPIRATORY PROTECTION FOR ETHYL FORMATE

Condition	Minimum Respiratory Protection* Required Above 100 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 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.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYLIDENE NORBORNENE

INTRODUCTION

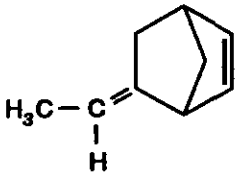
This guideline summarizes pertinent information about ethylidene norbornene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations 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_{12}

- **Structure**



- **Synonyms**

  5-Ethylidene-2-norbornene; 5-ethylidenebicyclo(2,2,1)hept-2-ene; ENB

- **Identifiers**

  1. CAS No.: 16219-75-3
  2. RTECS No.: RB9450000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Ethylidene norbornene is a combustible, colorless to white liquid with a turpentine-like odor. An odor threshold for ethylidene norbornene has been reported in the range of 0.007 to 0.014 parts per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 120.2
  2. Boiling point (760 mm Hg): 147.6°C (298°F)
  3. Specific gravity (water = 1): 0.896 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of ethylidene norbornene): 4.1
  5. Freezing/Melting point: -80°C (-112°F)
  6. Vapor pressure at 20°C (68°F): 4.2 mm Hg
  7. Solubility: Data not available
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, and oxygen.

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2. Incompatibilities: Contact of ethylidene norbornene with oxygen can cause violent reactions.

3. Hazardous decomposition products: Toxic gases (such as carbon dioxide) may be released in a fire involving ethylidene norbornene.

4. Special precautions: Because of its reactivity, ethylidene norbornene must be stabilized with tert-butyl catechol.

- **Flammability**

The National Fire Protection Association has not assigned a fire hazard rating for ethylidene norbornene; however, other sources report that this substance is combustible.

1. Flash point: 38.33°C (101°F) (open cup)

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, alcohol foam, or carbon dioxide to fight fires involving ethylidene norbornene. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving ethylidene norbornene 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. 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 ethylidene norbornene.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for ethylidene norbornene [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 (25 mg/m^3) as a ceiling limit for ethylidene norbornene. The ceiling limit should not be exceeded during any part of the workday [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned ethylidene norbornene a ceiling limit value of 5 ppm (25 mg/m^3), which should not be exceeded during any part of the working exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of eye and skin irritation associated with ethylidene norbornene exposure and renal, urogenital, and bone marrow effects found in animals exposed to ethylidene norbornene [NIOSH 1992]. The ACGIH limit is based on the risk of eye and nose irritation associated with exposure to ethylidene norbornene [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Ethylidene norbornene causes irritation of the eyes and skin, as well as liver and testicular toxicity in animals. In contact with the skin of rabbits, ethylidene norbornene caused a mild degree of skin irritation [NIOSH 1994]. The dermal LD_{50} in rabbits is 8,189 mg/kg [NIOSH 1994]. In contact with the eyes of rabbits, this substance produced transient conjunctival irritation [Grant 1986]. The 4-hr LC_{50} is 1,246 ppm in rats and 732 ppm in mice [NIOSH 1994]. The oral LD_{50} is 2,527 mg/kg in rats and 3,250 mg/kg in mice. Dogs exposed to a 93-ppm concentration of ethylidene norbornene for 7 hours/day, 5 days/week, for a total of 89 exposures showed slight blood changes and, at autopsy, hepatic lesions and testicular atrophy [Hathaway et al. 1991]. When dogs were exposed to a concentration of 61 ppm on the same regimen, less severe lesions of these organs were seen at post mortem. At an ethylidene norbornene concentration of 22 ppm, no damage was noted [Hathaway et al. 1991]. Twenty-one of twenty-four rats inhaling a 237-ppm concentration of ethylidene norbornene on the same schedule died. Liver

lesions, atrophy of the testicles, and hydrothorax were observed. No deaths occurred from 90 ppm, but liver lesions were evident [ACGIH 1991].

2. *Effects on Humans:* Ethylidene norbornene causes eye, nose, and upper respiratory tract irritation in humans. Volunteers exposed for 30 minutes to a 6-ppm concentration of ethylidene norbornene reported transient eye irritation, and, at a concentration of 11 ppm, both eye and nose irritation were experienced [ACGIH 1991]. In contact with the skin, ethylidene norbornene caused reddening and defatting [USCG 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to ethylidene norbornene include redness and inflammation of the eyes and eyelids, runny nose, scratchy throat, and redness and inflammation of the skin.

2. *Chronic exposure:* Repeated exposure to ethylidene norbornene may damage the liver, kidneys, and lungs in humans.

- **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 exposures to concentrated solutions, vapors, mists, or aerosols of ethylidene norbornene. ***Immediately and thoroughly*** flush eyes with large amounts of water occasionally lifting the lower and upper 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 ethylidene norbornene 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 ethylidene norbornene and may lead to worker exposures to this substance:

—Manufacture of pharmaceuticals and pesticides

—Preparation of specialty resins

—Use as the third monomer in ethylene-propylene diene monomer elastomers

The following methods are effective in controlling worker exposures to ethylidene norbornene, 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 ethylidene norbornene, 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, upper respiratory tract, reproductive system, skin, liver, and kidneys. 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 ethylidene norbornene at or below the prescribed exposure limit. A 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, respiratory tract, skin, liver, or kidneys or disturbances in reproductive 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 ethylidene norbornene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of ethylidene norbornene on the eyes, respiratory tract, skin, liver, kidneys, or reproductive function. 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 ethylidene norbornene.

- **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

No sampling and analytical method is available to determine a worker's exposure to airborne ethylidene norbornene.

PERSONAL HYGIENE

If ethylidene norbornene 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 ethylidene norbornene 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 ethylidene norbornene, particularly its potential to be irritating to the skin.

A worker who handles ethylidene norbornene 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 ethylidene norbornene or a solution containing ethylidene norbornene is handled, processed, or stored.

STORAGE

Ethylidene norbornene 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]. Ethylidene norbornene must be stored under an inert (oxygen free) atmosphere (i.e., a nitrogen atmosphere) or be stabilized with tert-butyl catechol. Containers of ethylidene norbornene should be protected from physical damage and should be stored away from oxygen, heat, sparks, and open flame. Because containers that formerly contained ethylidene norbornene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving ethylidene norbornene, 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. 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 ethylidene norbornene 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**

  Ethylidene norbornene 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 ethylidene norbornene; 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 ethylidene norbornene 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 ethylidene norbornene 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 ethylidene norbornene 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 ethylidene norbornene. 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 ethylidene norbornene 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 ethylidene norbornene.

Safety glasses, goggles, or face shields should be worn during operations in which ethylidene norbornene 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 ethylidene norbornene. Contact lenses should not be worn if the potential exists for ethylidene norbornene exposure.

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ETHYL MERCAPTAN

INTRODUCTION

This guideline summarizes pertinent information about ethyl 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_2H_5SH
- **Structure:** $CH_3—CH_2—SH$

- **Synonyms:** Ethanethiol, ethyl sulfhydrate, ethyl thiolalcohol, thioethanol, thioethyl alcohol
- **Identifiers:** CAS 75-08-1; RTECS DI9625000; DOT 2363, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a penetrating odor like garlic or decayed cabbage

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 62.13
2. Boiling point (at 760 mmHg): 35°C (95°F)
3. Specific gravity (water = 1): 0.839
4. Vapor density (air = 1 at boiling point of ethyl mercaptan): 2.1
5. Melting point: -148°C (-234°F)
6. Vapor pressure at 20°C (68°F): 442 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 1.5
8. Evaporation rate (butyl acetate = 1): 24.9
9. Saturation concentration in air (approximate) at 20°C (68°F): 58.2% (582,000 ppm)
10. Ionization potential: 9.28 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., sulfur dioxide and carbon monoxide) may be released in a fire involving ethyl mercaptan.
3. Caution: Ethyl mercaptan will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: <−18°C (<0°F) (closed cup)
2. Autoignition temperature: 300°C (572°F)
3. Flammable limits in air, % by volume: Lower, 2.8; upper, 18
4. Extinguishant: Carbon dioxide or dry chemicals for small fires, alcohol foam for large fires
5. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)

- **Warning properties**

1. Odor threshold: 0.26 to 0.97 ppb
2. Evaluation of warning properties for respirator selection: Because of its odor, ethyl 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 ethyl mercaptan is 10 parts of ethyl mercaptan per million parts of air (ppm) [25 milligrams of ethyl mercaptan per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.5 ppm (1.3 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®) is 0.5 ppm (1 mg/m^3) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for ethyl mercaptan

	Exposure limits	
	ppm	mg/m^3
OSHA PEL ceiling	10	25
NIOSH REL ceiling (15 min)	0.5	1.3
ACGIH TLV® TWA	0.5	1

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HEALTH HAZARD INFORMATION

• **Routes of exposure**

Ethyl mercaptan 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 ethyl mercaptan by rats and mice caused irritation of mucous membranes, incoordination, staggering gait, weakness, partial skeletal muscle paralysis, deficient oxygenation of the blood (cyanosis), respiratory depression, coma, and death. Sublethal doses produced swelling, fatty degeneration, and tissue destruction (necrosis) of the liver and cloudy swelling in the kidneys. Undiluted ethyl mercaptan instilled in the eyes of rabbits caused slight-to-moderate irritation. Chronic inhalation of ethyl mercaptan by rats and rabbits caused cardiovascular disorders, decreased gas exchange, increased nervous excitability, and effects on the blood-forming system including decreased red blood cell counts.

2. *Effects on humans:* Persons clinically exposed to low concentrations of ethyl mercaptan over a 5- to 10-day period reported an altered taste reaction to bitter and sweet substances and a rise in olfactory threshold.

• **Signs and symptoms of exposure**

Short-term (acute): Exposure to ethyl mercaptan can cause headache, nausea, weakness, fatigue, incoordination, and irritation of the 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, 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 ethyl 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 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 ethyl 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 skin and 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 ethyl 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 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 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 ethyl mercaptan. 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**

Currently there is no NIOSH-validated method for sampling and analysis of ethyl mercaptan. Detector tubes or other direct-reading devices calibrated to measure ethyl mercaptan may be used if available.

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 ethyl mercaptan.

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

SANITATION

Clothing which is contaminated with ethyl 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 ethyl mercaptan from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of ethyl 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 ethyl 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 ethyl 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 ethyl 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 ethyl mercaptan

Operations	Controls
During use as a fuel gas odorant	Process enclosure, general dilution ventilation, personal protective equipment
During use as a chemical intermediate or raw material in the production of insecticides, anti-oxidants, plastics, and pharmaceuticals	Process enclosure, general dilution ventilation, personal protective equipment
During use as a stabilizer (0.5 to 5% quantities for stabilizing synthetic resins, rubber, polyvinyl compounds, and adhesives)	Process enclosure, general dilution ventilation, personal protective equipment
During synthesis and processing of ethyl mercaptan	Process enclosure, general dilution ventilation, personal protective equipment
During use as a solvent for elastomeric polymers and oil soluble dyes in industrial stains and quicksetting rubber cements	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During 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 ethyl mercaptan, an eye-wash fountain should be provided within the immediate work area for emergency use.

If ethyl 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 ethyl mercaptan, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If ethyl mercaptan gets on the skin, wash it immediately with soap and water. If ethyl 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 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 ethyl 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 ethyl 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 ethyl mercaptan vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing ethyl mercaptan may be absorbed in vermiculite, dry sand, earth, or a similar material, treated with hypochlorite, and placed in an appropriate container. Ethyl mercaptan should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing ethyl 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 ethyl 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 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)
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
	Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
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
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 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 0.5 ppm (1.3 mg/m^3) (ceiling).

Occupational Health Guideline for n-Ethylmorpholine

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: $C_6H_{13}ON$
- Synonyms: 4-Ethylmorpholine
- Appearance and odor: Colorless liquid with an ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for N-ethylmorpholine is 20 parts of N-ethylmorpholine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 94 milligrams of N-ethylmorpholine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

n-Ethylmorpholine 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**

1. Short-term Exposure: n-Ethylmorpholine may cause irritation of the eyes, nose, and throat. Eye exposure may result in foggy vision and seeing halos around lights.

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 N-ethylmorpholine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to n-ethylmorpholine 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 n-ethylmorpholine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of N-ethylmorpholine might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: n-Ethylmorpholine is an eye irritant and has caused corneal edema in workers. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Liver disease: Although N-ethylmorpholine 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 N-ethylmorpholine 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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

n-Ethylmorpholine vapor causes visual disturbances and irritates mucous membranes. Some rats died after exposure to 2000 ppm for 4 hours. In an experimental study, humans exposed to 100 ppm for 2-½ minutes experienced irritation of eyes, nose, and throat, while 50 ppm produced lesser irritation. Workers exposed to low vapor concentrations for several hours reported temporarily fogged vision with rings around lights; corneal edema was observed; this effect is thought to 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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when air concentrations of substituted morpholines are 40 ppm or higher; the symptoms usually appear at the end of the work day and clear within 3 to 4 hours after cessation of exposure. The liquid when placed into the eye of a rabbit caused corneal haziness, sloughing, and irregularities of the surface, characteristic of severe desiccation. On the skin of a rabbit, the undiluted liquid produced no reaction, unlike unsubstituted morpholine, which is a severe skin irritant.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 115.2
2. Boiling point (760 mm Hg): 138.6 C (281 F)
3. Specific gravity (water = 1): 0.91
4. Vapor density (air = 1 at boiling point of N-ethylmorpholine): 4.0
5. Melting point: −63 C (−81 F)
6. Vapor pressure at 20 C (68 F): 5 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): 0.8

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid N-ethylmorpholine with strong acids will cause violent spattering. Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as ammonia, oxides of nitrogen, and carbon monoxide) may be released in a fire involving N-ethylmorpholine.
4. Special precautions: Liquid N-ethylmorpholine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 32.2 C (90 F) (closed cup)
2. Autoignition temperature: 185 C (365 F)
3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 9.8
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, in a study with human volunteers, the ammonia odor of N-ethylmorpholine is noticeable at 25 ppm. The odor becomes stronger at higher concentrations, but olfactory fatigue occurs.
2. Eye Irritation Level: Grant reports the occurrence of "transient edema of the corneal epithelium in workers exposed to 40 ppm or more in air during the work day."

The *Documentation of TLV's* reports that eye irritation was noted in human volunteers exposed to 100 ppm N-ethylmorpholine for 2-½ minutes. "Slight if any irritation" occurred at 50 ppm.

3. Other Information: The *Documentation of TLV's* reports that nose and throat irritation also occurred among human volunteers exposed to 100 ppm N-ethylmorpholine for 2-½ minutes. "Slight if any irritation" occurred at 50 ppm.
4. Evaluation of Warning Properties: Since olfactory fatigue occurs during exposure to N-ethylmorpholine, odor is not considered to be a good warning property. In addition, since irritation does not definitely occur until a concentration several times greater than the permissible exposure limit, N-ethylmorpholine 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 N-ethylmorpholine in an adsorption tube containing silica gel, followed by desorption with sulfuric acid, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure N-ethylmorpholine may be used. An analytical method for N-ethylmorpholine 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 N-ethylmorpholine.

• Clothing contaminated with N-ethylmorpholine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of N-ethylmorpholine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the N-ethylmorpholine, the person performing the operation should be informed of N-ethylmorpholine's hazardous properties.

• Where exposure of an employee's body to liquid N-ethylmorpholine 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 N-ethylmorpholine should be removed promptly and not reworn until the N-ethylmorpholine is removed from the clothing.

• Any clothing which becomes wet with liquid N-ethylmorpholine should be removed immediately and not reworn until the N-ethylmorpholine 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 N-ethylmorpholine or solutions containing N-ethylmorpholine contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to N-ethylmorpholine or solutions containing more than 15% N-ethylmorpholine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with N-ethylmorpholine should be promptly washed or showered to remove any N-ethylmorpholine.

• Employees who handle liquid N-ethylmorpholine 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 N-ethylmorpholine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a catalyst for flexible, semi-flexible, and rigid polyurethane foam production	Local exhaust ventilation; personal protective equipment
Use in polymer technology as a promoter for resin surface curing, and as a stabilizer for fiber spinning solutions	Local exhaust ventilation; personal protective equipment
Use in manufacture of vat dyes; use in manufacture of pharmaceuticals in purification of Penicillin G	Local exhaust ventilation; personal protective equipment
Use in organic synthesis as a special solvent, pH regulator, and for preparation of chemical intermediates	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 N-ethylmorpholine or solutions containing N-ethylmorpholine 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 N-ethylmorpholine gets on the skin, promptly flush the contaminated skin with water. If N-ethylmorpholine soaks through the clothing, remove the clothing immediately and flush the skin with water.

• **Breathing**

If a person breathes in large amounts of N-ethylmorpholine, 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 N-ethylmorpholine has 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. Under-

stand 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 N-ethylmorpholine 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. n-Ethylmorpholine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

n-Ethylmorpholine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on N-ethylmorpholine, look up N-ethylmorpholine 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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RESPIRATORY PROTECTION FOR N-ETHYLMORPHOLINE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Vapor Concentration	
1000 ppm or less	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 Health Guideline for Ethyl Silicate

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: $(C_2H_5O)_4Si$ or $(C_2H_5)_4SiO_4$
- Synonyms: Ethyl silicate, condensed; tetraethyl orthosilicate; tetraethyl silicate; ethyl orthosilicate tetraethoxysilane
- Appearance and odor: Colorless liquid with a mild, sweet, alcohol-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl silicate is 100 parts of ethyl silicate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 850 milligrams of ethyl silicate per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for ethyl silicate a Threshold Limit Value of 10 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ethyl silicate 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 ethyl silicate may irritate the eyes and nose. In animals, exposure to ethyl silicate has caused severe breathing difficulties, liver damage, kidney damage, and anemia. Repeated applications of ethyl silicate to animal skin has caused the skin to become dry.

- **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 ethyl silicate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ethyl silicate 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 ethyl silicate exposure.

—Chronic respiratory disease: Ethyl silicate causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl silicate might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Ethyl silicate 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: Ethyl silicate 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.

—Blood disease: Ethyl silicate causes anemia in animals. Persons with pre-existing blood disorders may be more susceptible to the effects of this agent.

—Skin disease: Ethyl silicate 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**

Ethyl silicate vapor irritates the eyes and nose and in animals causes lung, liver, and kidney damage. Exposure of guinea pigs to 2530 ppm for 4 hours was lethal to more than half of the animals; usually death was delayed and a result of pulmonary edema; effects were

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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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irritation of eyes and nose, lacrimation, tremor, dyspnea, and narcosis; some surviving animals later developed a delayed profound anemia. Exposure of rats to 1000 ppm for up to three 7-hour periods was fatal; autopsy findings were marked tubular degeneration and necrosis of the kidneys, mild liver damage, and slight pulmonary edema and hemorrhage. In rats exposed to 125 ppm for 15 to 20 7-hour periods, slight to moderate kidney damage was observed, but no pathologic changes were detected in the liver or lungs. In humans, the eyes and nose are affected by brief exposures as follows: 3000 ppm, extremely irritating and intolerable; 1200 ppm, lacrimation and stinging; 700 ppm, mild stinging; 250 ppm, slight tingling; Instillation of the liquid into the rabbit eye caused immediate marked irritation which was reversible. Repeated or prolonged skin contact with the liquid may cause dermatitis due to its solvent effect.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 169 C (336 F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of ethyl silicate): 7.2
5. Melting point: Less than −85 C (−121 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts slowly to form ethyl alcohol and silica gel
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: High temperatures may cause containers to explode.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with water causes formation of volatile and flammable ethyl alcohol.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl silicate.
4. Special precautions: Ethyl silicate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 37.2 C (99 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 1.3; Upper: 23
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: According to Grant, ethyl silicate can be detected by odor at 85 ppm.
2. Irritation levels: Grant states that "observations were made of the effect of various concentrations on the human experimenters: 3000 ppm was found to be extremely irritating to the eyes and nose; 1200 ppm stings eyes and nose and produces tears; 700 ppm mildly stings eyes and nose; 250 ppm makes the eyes and nose tingle slightly . . . ."
3. Evaluation of Warning Properties: Since the threshold of odor is below the permissible exposure limit, and since the thresholds of eye and nasal irritation are within three times the permissible exposure limit, ethyl silicate 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 packed with XAD-2 resin, followed by desorption with carbon disulfide and gas chromatographic analysis. Detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl silicate may be used. An analytical method for ethyl silicate 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 ethyl silicate.

• Clothing wet with liquid ethyl silicate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ethyl silicate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ethyl silicate, the person performing the operation should be informed of ethyl silicate's hazardous properties.

• Any clothing which becomes wet with liquid ethyl silicate should be removed immediately and not reworn until the ethyl silicate 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 ethyl silicate contacting the eyes.

SANITATION

• Skin that becomes wet with liquid ethyl silicate should be promptly washed or showered with soap or mild detergent and water to remove any ethyl silicate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl silicate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a bonding agent for investment castings, ceramic shells, crucibles, and types of refractory shapes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a protective coating for paints, lacquers, and films	General dilution ventilation; personal protective equipment
Use in manufacture of protective and preservative coatings for protection from corrosion, chemicals, heat, scratches, and fire	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in impregnation of porous materials to increase strength, hardness, stiffness, and abrasion	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a waterproofing and weatherproofing agent in porous rock	General dilution ventilation; personal protective equipment
Use as a chemical intermediate; use as a gelling agent in organic liquids; use as a coating agent inside electric lamp bulbs, and in the synthesis of fused quartz	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in textile industry in aqueous emulsions, deluster and fireproofing, and to increase strength; use as a component of lubricants as mold release agent	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 ethyl silicate 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 liquid ethyl silicate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid ethyl silicate 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 ethyl silicate, 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 ethyl silicate 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 ethyl silicate 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. Ethyl silicate 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 ethyl silicate vapors are permitted.

• Waste disposal methods:

Ethyl silicate 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 ETHYL SILICATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 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.
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 Health Guideline for Ferbam

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: $((CH_3)_2NCS_2)_3Fe$
- Synonyms: Ferric dimethyldithiocarbamate; tris(dimethyldithiocarbamato)iron
- Appearance and odor: Odorless black solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ferbam is 15 milligrams of ferbam 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 ferbam a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ferbam 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**

Ferbam dust may cause irritation of the eyes and respiratory tract. Swallowing large amounts of ferbam or liquids containing ferbam may cause gastrointestinal disturbances. Ferbam may also cause a skin rash in people who are allergic to sulfur.

- **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 ferbam.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ferbam 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 ferbam exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ferbam might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Ferbam can cause dermatitis. 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**

Ferbam dust irritates the eyes and respiratory tract. In guinea pigs given ferbam by stomach tube, the lethal range was 450 to 2000 mg/kg; the animals became stuporous and died in coma. Ten of 20 rats died from a diet containing 0.5% ferbam for 30 days; there was a slight and ill-defined tendency toward anemia; at autopsy there was no evidence of a regularly appearing tissue injury; minor abnormalities of the lung, liver, kidney and bone marrow were observed in a few animals. In humans, the dust is irritating to the eyes and respiratory tract; it causes dermatitis in individuals sensitized to sulfur. Large oral doses cause gastrointestinal disturbances. Because of chemical similarity to Antabuse, absorption of ferbam may potentiate action of ethyl alcohol.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 416.5
  2. Boiling point (760 mm Hg): Decomposes

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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3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of ferbam): Not applicable
5. Melting point: 180 C (356 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.012
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Temperatures above 180 C (356 F) cause decomposition with formation of toxic gases.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of sulfur and nitrogen and carbon monoxide) may be released in a fire involving ferbam.
4. Special precautions: None.

• **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperatures: 280 C (536 F) (cloud); 150 C (302 F) (layer)
3. Minimum explosive dust concentration: 0.055 g/l
4. Extinguishant: Water, dry powder

• **Warning properties**

Grant states that ferbam "is a fungicide, the dust of which is irritating to the eye, nose, throat, and skin."

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 ferbam 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 repeated or prolonged skin contact with ferbam or liquids containing ferbam.

• If employees' clothing may have become contaminated with ferbam or liquids containing ferbam, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with ferbam should be removed promptly and not reworn until the ferbam is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where ferbam or liquids containing ferbam may contact the eyes.

SANITATION

• Skin that becomes contaminated with ferbam should be promptly washed or showered with soap or mild detergent and water to remove any ferbam.

• Eating and smoking should not be permitted in areas where solid ferbam is handled, processed, or stored.

• Employees who handle ferbam or liquids containing ferbam 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 ferbam may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of fungicides	Process enclosure; local exhaust ventilation; personal protective equipment
Application as a foliage fungicide for control of scab and rust diseases	Personal protective equipment
Manufacture of ferbam	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 ferbam or liquids containing ferbam 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 ferbam or liquids containing ferbam get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If ferbam or liquids containing ferbam penetrate 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 ferbam, move the exposed person to fresh air at once.

• **Swallowing**

When ferbam or liquids containing ferbam 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 leaks until cleanup has been completed.

• If ferbam 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 ferbam should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Ferbam may be disposed of in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on ferbam, look up ferbam 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.

REFERENCES

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RESPIRATORY PROTECTION FOR FERBAM

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate Concentration	
75 mg/m³ or less**	Any dust respirator, except single-use.
150 mg/m³ or less**	Any dust 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.
7500 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 7500 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.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Ferrovanadium 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

- Formula: Ferrovanadium contains varying amounts of iron and vanadium and several other minor constituents (e.g., silicon, manganese, chromium, and nickel). Ferrovanadium has been produced with as little as 35% vanadium and as much as 85% vanadium.
- Synonyms: None
- Appearance: Dark, odorless solid particles.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ferrovanadium dust is 1 milligram of ferrovanadium dust (as vanadium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to 1 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Vanadium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ferrovanadium dust can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

Ferrovanadium dust causes irritation of the eyes, nose, and throat.

- **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 ferrovanadium dust.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ferrovanadium 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 and eyes should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ferrovanadium dust may cause respiratory impairment. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ferrovanadium dust is reported to cause asthmatic-like symptoms. 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.

- **Summary of toxicology**

Ferrovanadium dust is a mild irritant of the eyes and respiratory tract. Animals exposed for 1 hour on alternate days for 2 months to very high concentrations (1000 to 2000 mg/m^3) developed chronic bronchitis and pneumonitis. Workers exposed to unspecified concentrations developed a slight irritation of the eyes and respiratory tract. Systemic effects have not been reported from industrial exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: Not applicable
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 ferrovanadium dust): Not applicable

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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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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: Heat
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. Minimum ignition temperature: 400 C (752 F) (layer); 440 C (824 F) (cloud)
3. Minimum explosive concentration: 1.3 grams per cubic meter
4. Extinguishant: Dry sand, dry dolomite, dry graphite powder

• **Warning properties**

Ferrovanadium dust may cause 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 ferrovanadium dust, followed by chemical treatment and atomic absorption spectrophotometry. An analytical method for ferrovanadium dust 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.

SANITATION

• Eating and smoking should not be permitted in areas where ferrovanadium dust is generated in handling, processing, or storing of ferrovanadium.

• Employees who handle ferrovanadium 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 ferrovanadium dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture and processing of ferrovanadium alloy	General dilution ventilation; personal protective equipment
Use in the production of steel as an additive to produce grain refinement and hardenability	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 ferrovanadium dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists 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 ferrovanadium 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.

• **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 potentially hazardous amounts of ferrovanadium dust are inadvertently released, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of release to disperse the dust.
3. 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:

Ferrovanadium dust may be disposed of in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR FERROVANADIUM DUST

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
*Particulate Concentration	
5 mg/m³ or less	Any dust and mist respirator, except single-use 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 filter 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 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 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 Health Guideline for Fluorine

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: F_2
- Synonyms: None
- Appearance and odor: Pale yellow gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for fluorine is 0.1 part of fluorine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of fluorine per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for fluorine a Threshold Limit Value of 1 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Fluorine can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Exposure to fluorine gas may cause irritation of the eyes, nose, throat, lungs, and skin. It may cause severe breathing difficulties which may be delayed in onset. At high concentrations, as when coming directly from a gas cylinder, fluorine may cause severe burns of the eyes and skin. In animal experiments, exposure to fluorine has produced kidney and liver 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 fluorine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to fluorine 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 eyes, respiratory tract, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Fluorine causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEC (1 sec): Fluorine 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 by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Fluorine gas is a severe irritant of the eyes, mucous membranes, and skin. It reacts with water to produce ozone and hydrofluoric acid. The LC50 in mice for 60 minutes was 150 ppm; effects were irritation of the eyes and nose and the delayed onset of dyspnea and lethargy; autopsy findings included marked pulmonary congestion and hemorrhage. Mice exposed to sublethal concentrations had pulmonary irritation and delayed development of focal necrosis in the liver and kidneys. In humans the inhalation of high concentrations causes laryngeal spasm and bronchospasm, followed by the delayed onset of pulmonary edema; there may also be

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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gastrointestinal disturbances. Two human subjects found momentary exposure to 50 ppm intolerable; 25 ppm was tolerated briefly, but both subjects developed sore throat and chest pain which persisted for 6 hours. A blast of fluorine gas on the shaved skin of a rabbit caused a second-degree burn; lower concentrations cause severe burns of insidious onset resulting in ulceration, similar to those produced by hydrogen fluoride.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 38
2. Boiling point (760 mm Hg): −188 C (−307 F)
3. Specific gravity (water = 1): (Liquid) 1.5 at boiling point
4. Vapor density (air = 1 at boiling point of fluorine): 1.3
5. Melting point: −219 C (−363 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
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to burst.
2. Incompatibilities: Fluorine is a dangerously reactive gas. Contact with water causes formation of toxic hydrogen fluoride gas. It reacts vigorously with most oxidizable materials at room temperature, frequently with ignition. It reacts with nitric acid to form fluorine nitrate, which is an explosive gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride) may be released when fluorine decomposes.
4. Special precautions: Fluorine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but strong oxidizer.
2. Compressed gas cylinders containing fluorine should be stored in accordance with 29 CFR 1910.101.

- **Warning properties**

1. Odor Threshold: The *Hygienic Information Guide* for fluorine of the Commonwealth of Pennsylvania Division of Occupational Health states that fluorine "can be detected by odor in concentrations of only a few parts per million." Deichmann and Gerarde note that the odor is "sharp, penetrating, and characteristic."
2. Eye Irritation Level: Grant states that "exposure of human volunteers to fluorine in air showed that, although it caused very little irritation up to 25 ppm, it caused much irritation of the eyes and nose at 100 ppm. However, there were no aftereffects from exposure of the eyes to 100 ppm for one-half minute. Contact with high concentrations of fluorine gas or liquefied fluorine would presumably be extremely destructive."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds are not within three times the permissible exposure limit, fluorine 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 fluorine 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 fluorine, and to prevent skin from becoming frozen from contact with vessels containing liquid fluorine.
- Where there is any possibility of exposure of an employee's body to liquid fluorine, 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 liquid fluorine should be removed immedi-

ately and not reworn until the fluorine 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 fluorine contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid fluorine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid fluorine should be immediately washed or showered to remove any fluorine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to fluorine may occur and control methods which may be effective in each case:

Operation	Controls
Use during organic and inorganic synthesis in the production of fluorine compounds, refrigerants, plastics, incendiary devices, and electrolytic solvents	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a rocket fuel oxidizer for ammonia, hydrazine, hydrogen, JP-4, and diborane fuels at laboratories and test sites	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 fluorine or high concentrations of fluorine 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 fluorine or high concentrations of fluorine gas get on the skin, immediately flush the contaminated skin with water. If liquid fluorine or high concentrations of fluorine gas penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of fluorine, 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 fluorine 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.

REFERENCES

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RESPIRATORY PROTECTION FOR FLUORINE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
1ppm 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.
25 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
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 gas mask containing non-oxidizable sorbents and providing protection against fluorine. 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 fluorine; 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 Fluorotrichloromethane

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: CCl_3F
- Synonyms: Refrigerant 11; Freon 11; monofluorotrichloromethane; trichlorofluoromethane; trichloromonofluoromethane
- Appearance and odor: Colorless liquid or gas with a chlorinated-solvent odor that is detectable only at concentrations well above the permissible exposure (above 20% by volume).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for fluorotrichloromethane is 1000 parts of fluorotrichloromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5600 milligrams of fluorotrichloromethane 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 fluorotrichloromethane from 1000 ppm as a time-weighted average value to 1000 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Fluorotrichloromethane 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: Fluorotrichloromethane may cause drowsiness, unconsciousness, and death. Breathing high concentrations of this material may also cause the heart to beat irregularly or to stop suddenly.

2. Long-term Exposure: Prolonged overexposure to fluorotrichloromethane 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 fluorotrichloromethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to fluorotrichloromethane 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 fluorotrichloromethane exposure.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of fluorotrichloromethane might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Fluorotrichloromethane vapor is a narcotic and may cause asphyxia at high concentrations. The approximate lethal concentration for rats exposed for 4 hours was 66,000 ppm; guinea pigs exhibited stupor and incoordination after exposure to 50,000 ppm for 2 hours, while animals breathing concentrations of 22,000 ppm showed only occasional tremors. Repeated exposure of several species to 4,000 ppm for 7 hours daily resulted in no toxic effects. Sniffing aerosols of fluorochlorinated hydrocarbons has caused sudden death by cardiac arrest,

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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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probably due to sensitization of the myocardium. No instances of toxic effects from industrial exposure have been reported, but since the substance can dissolve the natural oils of the skin, dermatitis may be expected to result from repeated contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 137.4
  2. Boiling point (760 mm Hg): 23.8 C (74.8 F)
  3. Specific gravity (water = 1): 1.49
  4. Vapor density (air = 1 at boiling point of fluorotrichloromethane): 4.7
  5. Melting point: −111 C (−168 F)
  6. Vapor pressure at 20 C (68 F): 690 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.11
  8. Evaporation rate (butyl acetate = 1): 63
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Fluorotrichloromethane reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and hydrogen fluoride) may be released when fluorotrichloromethane decomposes.
  4. Special precautions: Liquid fluorotrichloromethane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**

According to Patty, fluorotrichloromethane is odorless; therefore, for the purposes of this guideline, it is treated as a material with poor warning properties.

Fluorotrichloromethane is not a known 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**

At the time of publication of this guideline, no measurement method for fluorotrichloromethane 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 repeated or prolonged skin contact with liquid fluorotrichloromethane.
- Non-impervious clothing which becomes wet with liquid fluorotrichloromethane should be removed promptly and not reworn until the fluorotrichloromethane has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid fluorotrichloromethane may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to fluorotrichloromethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a propellant in aerosols for insecticides, floor waxes, paint, cosmetics, and perfumes	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a refrigerant; as a blowing agent in foam plastics; as a solvent and degreaser; in production of polymeric	General dilution ventilation; local exhaust ventilation; personal protective equipment

resins; as a dielectric fluid in bubble chambers, and in wind tunnels; use as a sulfonation solvent in chemical synthesis

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 fluorotrichloromethane 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 immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid fluorotrichloromethane gets on the skin, immediately flush the contaminated skin with water if the liquid fluorotrichloromethane has already evaporated. If liquid fluorotrichloromethane soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of fluorotrichloromethane, 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 immediately.

• **Swallowing**

When fluorotrichloromethane 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 until cleanup has been completed.

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

1. Ventilate area of spill or leak.
2. If the gas is leaking, stop the flow of gas.
3. If in the liquid form, allow to vaporize.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Fluorotrichloromethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR FLUOROTRICHLOROMETHANE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
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 HEALTH GUIDELINE FOR FORMALDEHYDE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about formaldehyde 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:** CH_2O
- **Structure:** $CH_2=O$
- **Synonyms:** Formalin, methanal, methyl aldehyde, methylene glycol, methylene oxide, morbicid, paraform, superlysoform
- **Identifiers:** CAS 50-00-0; RTECS LP8925000; DOT 1198 and 2209, label required: "Combustible Liquid"
- **Appearance and odor:** Colorless gas with a pungent and irritating odor at ambient temperatures; also, commercially available at 30% to 55% formaldehyde in aqueous solution (formalin)

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 30.03
2. Boiling point (at 760 mmHg): -19.5°C (-3.06°F); 98°C (208°F) for 37% formaldehyde (15% methanol)
3. Specific gravity at 20°C (water = 1): 0.815; 1.075-1.081 for 37% formaldehyde (15% methanol)
4. Vapor density (air = 1 at boiling point of formaldehyde): 1.07
5. Melting point: -92°C (-133.5°F); -15°C (5°F) for 37% formaldehyde (15% methanol)
6. Vapor pressure at -88°C (-126.3°F): 10 mmHg
7. Soluble in water
8. Ionization potential: 10.88 eV

- **Reactivity**

1. Incompatibilities: Formaldehyde reacts violently with strong oxidants and alkaline materials.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving formaldehyde.
3. Caution: Formaldehyde should not be stored in confined spaces or near open flames, and containers should be protected from physical damage. Formaldehyde may react with hydrogen chloride to form bis-chloromethyl ether, a carcinogen.

- **Flammability**

1. Flash point: 50°C (122°F) for 37% formaldehyde (15% methanol) (closed cup); 85°C (185°F) for 37% formaldehyde (methanol free) (closed cup)
2. Autoignition temperature: 430°C (806°F) for 37% formaldehyde (methanol free)
3. Flammable limits in air, % by volume: Lower, 7; upper, 73
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide, or water spray (mist)
5. Class II Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA) for 37% formaldehyde (15% methanol); Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA) for 37% formaldehyde (methanol free)

- **Warning properties**

1. Odor threshold: 0.8 ppm
2. Eye irritation levels: In acclimated workers, mild to unpleasant irritation occurs at 2-10 ppm, and intolerable irritation (tissue damage possible) occurs at levels above 25 ppm.
3. 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 formaldehyde is 1 part of formaldehyde per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the OSHA short-term exposure limit (STEL) is 2 ppm for any 15-minute sampling period (see 29 CFR 1910.1048). The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 0.016 ppm [0.02 milligram of formaldehyde per cubic meter of air (mg/m^3)] as an 8-hour TWA and 0.1 ppm (0.15 mg/m^3) as a ceiling concentration determined in any 15-minute sampling

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period. This REL represents the lowest reliably quantifiable concentration at the present time. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated formaldehyde as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 1 ppm (1.5 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 2 ppm (3 mg/m³) (Table 1).

Table 1.—Occupational exposure limits for formaldehyde

	Exposure Limits	
	ppm	mg/m³
OSHA PEL TWA	1	—
STEL (15 min)	2	—
NIOSH REL TWA (Ca)*	0.016	0.02
Ceiling (15 min)	0.1	0.12
ACGIH TLV® TWA (A2)†	1	1.5
STEL (A2)	2	3

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure
Formaldehyde may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology
1. *Effects on animals:* Chronic inhalation of formaldehyde by rats produced cancer of the nasal cavity.
2. *Effects on humans:* Acute inhalation of formaldehyde has caused bronchitis, pulmonary edema, pneumonitis, pneumonia, and death due to respiratory failure. Formaldehyde solutions have caused eye burns, permanent corneal opacification, and loss of vision.

Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to formaldehyde gas can cause irritation of the eyes and respiratory tract, tearing, coughing, dry throat, tightening of the chest, headache, sensation of pressure in the head, and palpitations of the heart. Ingestion of formaldehyde can cause irritation of the mouth, throat, and stomach, nausea, vomiting, convulsions, and coma.
2. *Long-term (chronic):* Exposure to formaldehyde can cause dermatitis and sensitization of the skin and respiratory tract.

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 formaldehyde, 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 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 formaldehyde. 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 of chronic skin disease, concurrent dermatitis, and significant breathing impairment due to preexisting chronic lung disease. Skin patch testing with formaldehyde 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 formaldehyde. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an ex-

cessive decrease or adverse trend in the physiologic function of the eyes, 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 pre- and post-shift tests of lung function. Because formaldehyde gas is rapidly metabolized to naturally occurring compounds in the nasopharyngeal tissues and therefore does not accumulate in the blood, biologic monitoring would not be effective in detecting the presence of formaldehyde or its metabolites in the blood or urine.

• 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 formaldehyde 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: Extrinsic asthma and allergic and/or contact dermatitis.
2. Delayed-onset SHE's include: Extrinsic asthma.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to formaldehyde 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 formaldehyde. 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 formaldehyde with solid sorbent tubes filled with 2-(benzylamino) ethanol on Chromosorb 102 or XAD-2, followed by desorption with isooctane, ultrasonic bath, or shaking, and analyzing by using a gas chromatograph with a hydrogen-air flame ionization detector. Direct reading devices calibrated to measure formaldehyde may also be used if available. A detailed sampling and analytical method for formaldehyde may be found in the *NIOSH Manual of Analytical Methods* (method number 2502).

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 formaldehyde.

SANITATION

Clothing which is contaminated with formaldehyde 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 formaldehyde from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of formaldehyde'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 formaldehyde 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 formaldehyde 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 formaldehyde 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 formaldehyde

Operations	Controls
During the synthesis and handling of formaldehyde resins; during the synthesis of chelating agents and dyes	Process enclosure, local exhaust ventilation, personal protective equipment
During use in textile manufacturing and handling and in tanning operations	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture of particle board, soft wood plywood, sandpaper, and grinding wheels	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an embalming fluid	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 formaldehyde, an eye-wash fountain should be provided within the immediate work area for emergency use.

If formaldehyde 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 formaldehyde, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If formaldehyde gets on the skin, wash it immediately with soap and water. If formaldehyde 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 formaldehyde is spilled or leaked, the following steps should be taken:

1. If formaldehyde is in the gaseous form, stop the flow of 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. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing formaldehyde, absorb on paper towels and place in an appropriate container.
5. Large quantities of liquids containing formaldehyde may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
6. Liquids containing formaldehyde may be collected by vacuuming with an appropriate system. If a vacuum system is used to remove formaldehyde, 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 enviromental 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 formaldehyde

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 Formic Acid

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: HCOOH
- Synonyms: Formic acid 85%; formic acid 90%; formic acid 95%; hydrogen carboxylic acid; methanoic acid
- Appearance and odor: Colorless liquid that may fume with a pungent, penetrating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for formic acid is 5 parts of formic acid per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 9 milligrams of formic acid per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Formic acid 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: Formic acid may cause irritation of the eyes, nose, throat, upper respiratory tract, and skin. These are often accompanied by watering of the eyes, nasal discharge, and coughing. Skin contact with concentrated solutions causes severe irritation and blistering. Swallowing formic acid has caused a number of cases of severe poisoning and death. The symptoms found in this type of poisoning include salivation, vomiting, burning sensation of the mouth, bloody vomiting, diarrhea, and pain. In severe poisoning, the person may go into shock. Later, the person may have trouble breathing and may die. The person may also have kidney damage. One death has been reported in a worker who had hot formic acid splashed in his face. This worker could not speak, had trouble breathing, and died six hours later.

2. Long-term Exposure: Prolonged or repeated exposure to formic acid 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 formic acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to formic acid 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 formic acid exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of formic acid might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Formic acid is a primary skin irritant and has caused skin sensitization. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although formic acid 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.

—Liver disease: Although formic acid 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.

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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—Eye disease: Formic acid is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems 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**

Formic acid vapor is a severe irritant of the eyes, mucous membranes, and skin. Exposure causes eye irritation with lacrimation, nasal discharge, throat irritation, and cough. A worker splashed in the face with hot formic acid developed marked dyspnea with dysphagia, and died within 6 hours. Workers exposed to a mixture of formic and acetic acids at an average concentration of 15 ppm of each complained of nausea. The liquid on the skin causes burns with vesiculation; keloid formation at the site of the burn often results. Skin sensitization may occur in persons previously exposed to formaldehyde. While ingestion of the liquid is unlikely in ordinary industrial use, the highly corrosive nature of the substance may be expected to produce serious burns of the mouth and esophagus.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 46.03
2. Boiling point (760 mm Hg): 85%: 107 C (224.6 F); 90%: 106.5 C (223.7 F); 95%: 102 C (215.6 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of formic acid): 1.6
5. Melting point: 85%: −15.3 C (4.5 F); 90%: −6.5 C (20.3 F); 95%: 1.4 C (34.5 F)
6. Vapor pressure at 20 C (68 F): 23− 33 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): 2.1

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers or strong caustics may cause fires and explosions. Contact with concentrated sulfuric acid causes formation of toxic and flammable carbon monoxide gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving formic acid.
4. Special precautions: Liquid formic acid will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point (90% solution): 50 C (122 F) (closed cup)
2. Autoignition temperature (90% solution): 435 C (813 F)
3. Flammable limits in air, % by volume: Lower: 18; Upper: 57
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: May reports an odor threshold of 21 ppm. Patty states that formic acid has a "pungent, penetrating" odor.
2. Eye Irritation Level: Grant notes,'It has been said that the vapors of formic acid are irritating to the eyes . . ., but there appears to be little in the literature on this subject." According to Patty, "the principal hazard is that of severe primary damage to the skin, eye, or mucosal surfaces." Deichmann and Gerarde also state that formic acid is irritating to the eyes.
3. Other Information: Grant, Patty, and Deichmann and Gerarde report that formic acid is a mucous membrane irritant, capable of irritating the upper respiratory tract and the eyes. The *Documentation of TLV's* states that "workers exposed to formic and acetic acids in a textile plant . . . at concentrations of each acid averaging 15 ppm" experienced irritation at these levels.
4. Evaluation of Warning Properties: Through its odor and irritant effects, formic acid is detectable at concentrations only several times the permissible exposure limit. For the purposes of this guideline, therefore, formic acid is judged 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**

Sampling and analyses may be performed by collection of formic acid on chromosorb 103, desorption with deionized water, and analysis by ion chromatography. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure formic acid may be used. An analytical method for formic acid 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 formic acid.

• Clothing contaminated with formic acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of formic acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the formic acid, the person performing the operation should be informed of formic acid's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid formic acid, 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 formic acid should be removed immediately and not reworn until the formic acid 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 formic acid or solutions containing formic acid contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid formic acid or solutions containing 1% or more of formic acid by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with formic acid should be immediately washed or showered to remove any formic acid.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to formic acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in textile dyeing and finishing industry as a dye exhausting agent; chrome dyeing; to impart finishes to cotton; an acidifying agent; and shrink- and wrinkle-proofing compound	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate as a strong reducing agent for acids, salts, dyes, fumigants, refrigerants, pharmaceuticals, and solvents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in leather processing industry as a deliming agent and neutralizer; as a preservative and levelling agent	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber industry as a coagulant for natural rubber latex and form making; as a preservative of latex	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst in hydrocarbon-formaldehyde resins and phenolic resins, and plasticizer for vinyl resins	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in electroplating industry to control particle size and plating thickness	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an antiseptic in wine and beer brewing, preservative in animal feed additives and cleaning solution compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous operations as a wire stripping compound and preparing bare wires for soldering; laundry sour; and as an oil well acidifying agent	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 formic acid or solutions containing formic acid 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 formic acid gets on the skin, immediately flush the contaminated skin with water. If formic acid soaks 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 formic acid, 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 formic acid has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the formic acid. 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, 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 formic acid 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. Formic acid should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Formic acid 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 FORMIC ACID

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor of Particulate Concentration	
100 ppm or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 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 Furfural

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_3OCHO
- Synonyms: 2-Furaldehyde; furfuraldehyde; fural; 2-furancarboxaldehyde
- Appearance and odor: Colorless to light brown liquid that darkens on standing in light and air. Odor is like almonds.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for furfural is 5 parts of furfural per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 20 milligrams of furfural 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 furfural from 5 ppm to 2 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Furfural 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: Furfural may cause irritation of the skin, eyes, and respiratory tract. It may also cause a person to become unconscious.

2. Long-term Exposure: Furfural may cause sensitization of the skin, loss of sense of taste, and numbness of the tongue.

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 furfural.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to furfural 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 furfural exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of furfural might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Skin disease: Furfural can cause dermatitis on excessive exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although furfural 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 furfural 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**

Furfural vapor is irritating to the eyes, respiratory tract, and skin. It has been reported to be a central nervous system poison in large doses in some animals, causing hyper-reflexia and convulsions.

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: 96
  2. Boiling point (760 mm Hg): 162 C (323 F)
  3. Specific gravity (water = 1): 1.16
  4. Vapor density (air = 1 at boiling point of furfural): 3.3
  5. Melting point: −36.5 C (−33.7 F)
  6. Vapor pressure at 20 C (68 F): 2 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 8.3
  8. Evaporation rate (butyl acetate = 1): Very low
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong acids and oxidizing materials may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving furfural.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 60 C (140 F) (closed cup)
  2. Autoignition temperature: 316 C (600 F)
  3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 19.3
  4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
- **Warning properties**
  1. Odor Threshold: The AIHA *Hygienic Guide* states that "although the odor threshold of furfural vapor has been reported to be 0.25 to 0.38 ppm, some industrial hygienists maintain that the odor becomes readily noticeable only near the TLV concentration of 5 ppm."
  2. Eye Irritation Level: Grant states that "chronic exposure to the vapor at concentrations of 13.5 ppm or less in air is reported to cause reddening of the eyes, tearing, and irritation of the throat in workers." The *Hygienic Guide* states that the "irritating properties of furfural, which become uncomfortable at 20 to 50 ppm, probably preclude voluntary exposures which might lead to significant injury."
  3. Nasal Irritation Level: The *Hygienic Guide* states that "nasal irritation would indicate that the TLV was being exceeded."
  4. Evaluation of Warning Properties: Through its odor and irritant effects, furfural can be detected near the permissible exposure limit. For the purposes of this guideline, therefore, furfural 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 furfural 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 furfural.
- Clothing contaminated with furfural should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of furfural from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the furfural, the person performing the operation should be informed of furfural's hazardous properties.
- Non-impervious clothing which becomes contaminated with furfural should be removed promptly and not reworn until the furfural is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid furfural may contact the eyes.

SANITATION

- Skin that becomes contaminated with furfural should be promptly washed or showered to remove any furfural.
- Employees who handle liquid furfural 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 furfural may occur and control methods which may be effective in each case:

Operation	Controls
Use during removal of industrial coatings in open-surface tanks	Local exhaust ventilation; personal protective equipment
Liberation during cold molding of abrasive grinding wheels	General dilution ventilation
Use in rubber of phenolic cement adhesives	General dilution ventilation; personal protective equipment
Liberation during molding of miscellaneous phenolic resin products	Local exahaust ventilation; general dilution ventilation
Use during molding of friction materials as brake linings, clutch facings, brake blocks, etc.	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of reinforced plastic products	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during coating of products with resins/varnishes as wire coating, food containers, paper, canvas, etc.	General dilution ventilation; process enclosure; local exhaust ventilation
Liberaiton during vulcanization of rubber in processes using furfural as an accelerator	General dilution ventilation; process enclosure; local exhaust ventilation
Liberation during manufacture of furfuryl alcohol	Process enclosure; general dilution ventilation
Liberation during use as a chemical intermediate in manufacture of furor, tetrahydrofuran, tetrahydrofuryl alcohol, hexamethylene diamene, and pyromucic acid	General dilution ventilation
Liberation during manufacture of phenolic-furfural resins; during dewaxing of oils, primarily lubricating oils; during decolorization of wood resins	Process enclosure; general dilution ventilation
Use during manufacture of surface coatings	General dilution ventilation; process enclosure; local exhaust ventilation
Liberation during separation of butadiene, benzene, and miscellaneous compounds from C_4 hydrocarbons; during manufacture of some polyurethane elastomers	Process enclosure; general dilution ventilation
Use during in situ desludging and decarbonizing of internal combustion engines	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 furfural 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 furfural gets on the skin, promptly flush the contaminated skin with water. If furfural 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 furfural, 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 furfural 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 furfural 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. For large quantities, cover with sodium bisulfite ($NaHSO_3$), add a small amount of water and mix. Then, after one hour, flush with large amounts of water and wash site with soap solution.

• Waste disposal methods:

Furfural 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. For small quantities, by absorbing it in vermiculite, dry sand, earth, or a similar material and disposing it in a suitable combustion chamber.
3. For large quantities, by mixing with a flammable liquid (such as acetone) and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR FURFURAL

Condition	*Minimum Respiratory Protection** Required Above 5 ppm
Vapor Concentration	
250 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 fuil facepiece.
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.

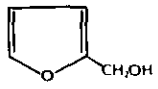
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR FURFURYL ALCOHOL

INTRODUCTION

This guideline summarizes pertinent information about furfuryl 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:** $C_5H_6O_2$
- **Structure:**



- **Synonyms:** 2-Furancarbinol, 2-furanmethanol, furfural alcohol, furyl alcohol, 2-furylcarbinol, 2-furylmethanol, 2-hydroxymethylfuran
- **Identifiers:** CAS 98-00-0; RTECS LU9100000; DOT 2874, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Colorless to pale yellow, syrupy liquid with a mild odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.10
2. Boiling point (at 760 mmHg): 170°C (338°F)
3. Specific gravity (water = 1): 1.1351
4. Vapor density (air = 1 at boiling point of furfuryl alcohol): 3.38
5. Melting point: -14.63°C (5.7°F)
6. Vapor pressure at 31.8°C (89°F): 1 mmHg
7. Miscible with water
8. Evaporation rate (butyl acetate = 1): Very slow
9. Saturation concentration in air (approximate) at 31.8°C (89°F): 0.13% (1,300 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong acids (including some organic acids) or acid catalysts may cause polymerization with the liberation of heat and violent spattering. Avoid contact with strong oxidizers.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving furfuryl alcohol.

3. Caution: Furfuryl alcohol will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: 77°C (170°F) (closed cup)
2. Autoignition temperature: 490°C (915°F)
3. Flammable limits in air, % by volume: Lower, 1.8; Upper, 16.3
4. Extinguishant: Alcohol foam, carbon dioxide, or dry chemical
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 7-8 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, furfuryl alcohol can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, furfuryl alcohol is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for furfuryl alcohol is 50 parts of furfuryl alcohol per million parts of air (ppm) [200 milligrams of furfuryl alcohol per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 50 ppm (200 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 10 ppm (40 mg/m^3) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek; and the ACGIH short-term exposure limit (STEL) is 15 ppm (60 mg/m^3) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the 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 furfuryl alcohol

	Exposure limits ppm	mg/m³
OSHA PEL TWA	50	200
NIOSH REL TWA	50	200
ACGIH TLV® TWA (Skin)*	10	40
STEL (Skin)	15	60

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

• Routes of exposure

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

• Summary of Toxicology

Effects on animals: Repeated daily exposure to mice, rats, or rabbits to furfuryl alcohol caused increased respiration, respiratory tract irritation, and vascular congestion, followed by decreased respiration, decreased force of cardiac contraction, decreased contractility of the gastrointestinal tract, drop in blood pressure, paralysis of sensory nerves, and death due to respiratory failure or possibly to cardiac arrest.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to furfuryl alcohol can cause excitement, drowsiness, nausea, vomiting, salivation, diarrhea, dizziness, shortness of breath, irregular breathing, and increased urination. Eye contact with furfuryl alcohol can cause redness, tearing, serious irritation, and corneal opacities; dermal contact can cause minor irritation.
2. *Long-term (chronic):* Exposure to furfuryl alcohol can cause headache, eye irritation, 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 furfuryl 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, cardiovascular, 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 furfuryl 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 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 furfuryl 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, and cardiovascular, 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 furfuryl 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 furfuryl alcohol 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 furfuryl alcohol may also be used if available. A detailed sampling and analytical method for furfuryl alcohol may be found in the *NIOSH Manual of Analytical Methods* (method number S365).

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 furfuryl alcohol.

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

SANITATION

Clothing which is contaminated with furfuryl alcohol 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 furfuryl alcohol from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of furfuryl 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 furfuryl 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 furfuryl 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 furfuryl 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 furfuryl alcohol

Operations	Controls
During the manufacture of cements, molded high-density carbon, and graphite articles; during the preparation of furfuryl-dimethylol urea and furan resins	Local exhaust ventilation, general exhaust ventilation, personal protective equipment
During the synthesis and handling of furfuryl alcohol; during use as a solvent; during use in impregnation of wood	Local exhaust ventilation, general exhaust ventilation, personal protective equipment
During use in sand consolidation for oil and gas recovery operations	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 furfuryl alcohol, an eye-wash fountain should be provided within the immediate work area for emergency use.

If furfuryl 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 furfuryl alcohol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If furfuryl alcohol gets on the skin, wash it immediately with soap and water. If furfuryl 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 furfuryl 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 furfuryl 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 furfuryl alcohol vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing furfuryl alcohol may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Furfuryl alcohol should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

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 furfuryl alcohol

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 250 ppm	Any powered air-purifying respirator with organic vapor cartridge(s) (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 supplied-air respirator (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)
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
	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 (200 mg/m³) (TWA).

Occupational Health Guideline for Glycidol

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: $C_3H_6O_2$
- Synonyms: 2-Hydroxymethyloxiran; hydroxymethyl ethylene oxide; epoxypropyl alcohol; glycide; 3-hydroxypropylene oxide; 2,3-epoxy-1-propanol
- Appearance: Colorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for glycidol is 50 parts of glycidol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 150 milligrams of glycidol per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Glycidol 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 glycidol may cause irritation of the eyes, nose, and throat.

2. Long-term Exposure: Prolonged overexposure might produce 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 glycidol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to glycidol 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 glycidol exposure.

—Skin disease: Glycidol is a primary skin irritant and can cause dermatitis on prolonged exposure. Persons 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 glycidol 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**

Glycidol vapor is an irritant to the eyes and upper respiratory tract, a skin irritant, and a central nervous system depressant. The LC50 for mice (4 hr) was 450 ppm, and for rats (8 hr), 580 ppm, resulting in pneumonitis; rats exposed at 400 ppm daily showed only slight eye irritation and mild respiratory distress, with no evidence of systemic toxicity. Lethal doses of 0.45 to 0.85 g/kg of the liquid administered by gastric tube resulted initially in nervous system depression, but surviving animals showed a reversal of the depressant effect, manifested by excitation and tremors. Direct application of the liquid to the skin of animals classifies glycidol as a moderate skin irritant; instilled into the eye, it is classified as a severe eye irritant. Exposure to near-saturated vapor for 8 hours resulted in corneal opacity. Repeated intramuscular injections do not affect hematopoiesis in rats. The only report of toxic effects in humans is that of irritation of the eyes, nose, and respiratory tract of experimenters working with the compound at room temperature.

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: 74
2. Boiling point (760 mm Hg): 166 C (331 F) (decomposes)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of glycidol): 2.6
5. Melting point: −45 C (−49 F)
6. Vapor pressure at 20 C (68 F): 0.9 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 strong oxidizing agents (especially nitrates) may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving glycidol.
4. Special precautions: Glycidol will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 72 C (162 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, alcohol foam

• **Warning properties**

1. Odor Threshold: No information is available concerning the odor threshold of glycidol.
2. Eye Irritation Level: Grant states, "In vapor form, glycidol has proven damaging to the corneas of rats, but for human beings the vapor has been found to have adequate warning properties, consisting of eye and respiratory irritation, to preclude excessive industrial exposure." The *Documentation of TLV's* states that following the first few exposures, "rats exposed at 400 ppm glycidol 7 hours a day for 50 days . . . (experienced) very slight irritation of the eyes, with slight lacrimation and encrustation of the eyelids . . . ." No quantitative information is available concerning the threshold of eye irritation.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of glycidol, 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 glycidol vapors using an adsorption tube with subsequent desorption with tetrahydrofuran and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure glycidol may be used. An analytical method for glycidol 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 glycidol.

• Clothing contaminated with liquid glycidol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of glycidol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the glycidol, the person performing the operation should be informed of glycidol's hazardous properties.

• Non-impervious clothing which becomes contaminated with liquid glycidol should be removed promptly and not reworn until the glycidol is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid glycidol may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid glycidol should be promptly washed or showered to remove any glycidol.
• Employees who handle liquid glycidol 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 glycidol may occur and control methods which may be effective in each case:

Operation	Controls
Use in surface coatings; use in chemical synthesis; use as a stabilizer for natural oils and vinyl polymers	General dilution ventilation; personal protective equipment
Use as a demulsifying agent; use as a dye leveling (retarding) agent	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 glycidol 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 glycidol gets on the skin, promptly wash the contaminated skin with water. If glycidol soaks through the clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing, get medical attention.
• **Breathing**
If a person breathes in large amounts of glycidol, 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 glycidol 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 glycidol 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, or absorbed in vermiculite, dry sand, earth, or a similar material and disposed in a sanitary landfill.
• Waste disposal method:
Glycidol may be disposed of by dissolving in petroleum and atomizing in a suitable combustion chamber, or absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a sanitary landfill.

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RESPIRATORY PROTECTION FOR GLYCIDOL

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
500 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 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 Natural Graphite

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
- Synonyms: Plumbago; potelot; carbo mineralis; black lead; carburet of iron; silver lead; crayon noir
- Appearance and odor: Black, greasy, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for natural graphite is 15 million particles of natural graphite per cubic foot of air (mppcf) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Natural graphite can affect the body if it is inhaled or if it comes in contact with the eyes.

- ***Effects of overexposure***

Repeated inhalation of natural graphite over a number of years may cause scarring of the lungs with such symptoms as chest tightness, shortness of breath, cough, black sputum, and pain.

- **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 natural graphite.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to natural graphite 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 the cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Natural graphite may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Natural graphite 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.

- **Summary of toxicology**

Natural graphite dust causes graphite pneumoconiosis. The earliest roentgenologic changes may be the disappearance of normal vascular markings, with the appearance later of pinpoint and macronodular densities in all lung fields. Massive lesions, when present, are caused by large cysts filled with black fluid. The pleura is often involved: hydrothorax, pneumothorax, and pleural thickening may occur. At autopsy, the lungs are gray-black to black; histologically there are widely scattered particles, spicules, and plates of graphite, often within intra-alveolar phagocytes amidst diffuse interstitial fibrosis and occasionally pneumonitis. There are also interwoven bands of collagen, similar to those found in silicosis, which frequently are the most prominent feature of the fibrotic lesions occupying the lung and the bronchial lymph nodes. Symptoms include expectoration of black sputum, dyspnea, and cough. It has been generally believed that the capacity of inhaled natural graphite dust to cause disease is largely the result of its crystalline silica component. However, there is a recent report of a worker who, after exposure to "nearly pure" carbon for 17 years as a grinder of synthetic graphite bars, developed cough, dyspnea, and reduced pulmonary function, and died. At autopsy, both ventricles of

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 heart were hypertrophied, and the lungs revealed the typical findings of graphite pneumoconiosis including fibrous tissue; the ashed material from the lung showed little or no birefringent particles, indicating the absence of silicious material.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 12
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 2.25
  4. Vapor density (air = 1 at boiling point of natural graphite): Not applicable
  5. Melting point: 3350 C (6040 F) (sublimes)
  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 very strong oxidizers such as fluorine, chlorine trifluoride, and potassium peroxide may cause fires and explosions.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Flash point: Not applicable
  2. Minimum ignition temperature: 730 C (1346 F) (cloud); 580 C (1076 F) (layer)
  3. Minimum explosive concentration: Data not available
  4. Extinguishant: Water
- **Warning properties**

Grant states that "carbon, when pure, has no toxic effect on the eye. As superficial foreign bodies, carbon black and graphite may be slightly irritating mechanically and may cause discoloration of lids and conjunctivae, but they are chemically inert."

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 graphite 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 natural graphite may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining, purification, packaging, blasting, and drilling	Local exhaust ventilation; personal protective equipment
Use in foundry facings; steelmaking as carbon raiser; manufacture of refractories in crucibles and retorts; use in manufacture of lubricants and adhesives in bearings, slides, gears, engines, and mold release agents	Process enclosure; local exhaust ventilation; personal protective equipment
Manufacture of writing and drafting agents; manufacture of industrial paints, inks, and polishes; manufacture of motor and generator brushes, batteries, carbon resistors, and electrodes	Process enclosure; local exhaust ventilation; personal protective equipment

Use in manufacture of tungsten carbide cutting tools, friction materials and clutch facings; use in electroplating; use in manufacture of ammunition; miscellaneous uses in hard rubber, engine packing, cord, rope, twine, floor coverings, and coatings for fertilizer	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 natural graphite 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.

• **Breathing**

If a person breathes in large amounts of natural graphite, 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 spills until cleanup has been completed.

• If natural graphite is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation, burning in a suitable combustion chamber or for disposal in a secured sanitary landfill.

• Waste disposal methods:

Natural graphite may be disposed of:

1. In a sanitary landfill.
2. By burning in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Graphite (Natural)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• Ranasinha, K. W., and Uragoda, C. G.: "Graphite Pneumoconiosis," *British Journal of Industrial Medicine,* 29:178-183, 1972.

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RESPIRATORY PROTECTION FOR NATURAL GRAPHITE

Condition	Minimum Respiratory Protection* Required Above 15 mppcf
Particulate Concentration	
75 mppcf or less	Any dust respirator.
150 mppcf or less	Any dust 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 mppcf 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.
7500 mppcf or less	A powered air-purifying respirator with a high efficiency filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7500 mppcf 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 Hafnium and Compounds (as Hafnium)

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 hafnium and compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Hafnium

- Formula: *Hf*
- Synonyms: Hafnium, metallic; hafnium, elemental
- Appearance: Gray solid

Hafnium tetrachloride

- Formula: $HfCl_4$
- Synonyms: None
- Appearance and odor: White solid with an acrid odor in moist air.

Hafnium oxychloride

- Formula: $HfOCl_2$ $8H_2O$
- Synonyms: Hafnium oxychloride octahydrate
- Appearance and odor: White, odorless solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hafnium and compounds (as hafnium) is 0.5 milligram of hafnium and compounds (as hafnium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hafnium, hafnium tetrachloride, or hafnium oxychloride 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**

Exposure to hafnium salts has caused irritation of the eyes and skin in animals. Hafnium chloride has caused liver damage in animals on prolonged feeding.

- **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 hafnium and compounds (as hafnium).

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to hafnium and compounds at potentially hazardous levels. The employer should screen employees for history of liver disease. Hafnium compounds have been reported to cause 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. Only those giving a postive history of these conditions should be referred for further medical examinations.

- **Summary of toxicology**

Hafnium and its compounds have been reported to cause liver damage in animals. The LD50 of hafnium, chiefly as the oxychloride, was 76 mg Hf/kg for mice. A 90-day hafnium chloride feeding study in rats at 1.0% and 0.1% resulted in unspecified liver effects. Studies with radioactive Hf mandelate indicate slow elimination from the body. Some compounds may cause irritation of eyes, skin, and mucous membranes.

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

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

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Hafnium**

1. Molecular weight: 178.5
2. Boiling point (760 mm Hg): 3100 C (5612 F) approximately
3. Specific gravity (water = 1): 13.3
4. Vapor density (air = 1 at boiling point of hafnium): Not applicable
5. Melting point: 2227 C (4040 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data —Hafnium tetrachloride**

1. Molecular weight: 320.3
2. Boiling point (760 mm Hg): 317 C (603 F)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of hafnium tetrachloride): Not applicable
5. Melting point: 432 C (809 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Hafnium oxychloride**

1. Molecular weight: 409.5
2. Boiling point (760 mm Hg): Decomposes (data not available)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of hafnium oxychloride): Not applicable
5. Melting point: Less than 50 C (less than 122 F)
6. Vapor pressure at 20 C (68 F): Very low
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: Contact of hafnium metal with chlorine and 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 hafnium, hafnium tetrachloride, or hafnium oxychloride.
4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Hafnium: Data not applicable; hafnium tetrachloride and hafnium oxychloride: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Hafnium: Water; hafnium tetrachloride and hafnium oxychloride: Not applicable

• **Warning properties**

Hafnium is not known to be an eye irritant; however, Haley reports that hafnium compounds may prove irritating to the mucosal surfaces.

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 hafnium and compounds 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 wet or dry hafnium powder. The clothing should be flame-resistant and should be treated or should be of a type so as to minimize the static electricity hazard of ignition.

• 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 hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds, where skin contact may occur.

• If employees' clothing has had any possibility of being contaminated with wet or dry hafnium powder, employees should change into uncontaminated clothing before leaving the work premises.

• If employees' clothing may have become contaminated with hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with wet or dry hafnium powder should be placed in fireproof closed containers for storage until it can be discarded or until provision is made for the removal of hafnium from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hafnium, the person performing the operation should be informed of hafnium's hazardous properties.

• Clothing contaminated with hafnium tetrachloride or hafnium oxychloride 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 there is any possibility of exposure of an employee's body to wet or dry hafnium powder, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Where exposure of an employee's body to hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Any clothing which becomes contaminated with wet or dry hafnium powder should be removed promptly but in a careful and cautious manner so as to reduce the probability of ignition by friction, static electricity, or other causes. Such clothing should not be reworn until the hafnium is removed from the clothing.

• Non-impervious clothing which becomes wet with hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds 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 wet or dry hafnium powder, hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to wet or dry hafnium powder, hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Workers subject to skin contact with wet or dry hafnium powder should wash any areas of the body which may have contacted hafnium powder at the end of each work day.

• Skin that becomes wet with wet or dry hafnium powder should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.

• Skin that becomes contaminated with hafnium tetrachloride, hafnium oxychloride, or liquids these compounds should be promptly washed or showered to remove any contaminant.

• Eating and smoking should not be permitted in areas where wet or dry hafnium powder, hafnium tetrachloride, or solid hafnium oxychloride or liquids containing these compounds are handled, processed, or stored.

• Employees who handle hafnium or its compounds or liquids containing hafnium or its compounds 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 hafnium and compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining and purification of hafnium (separation from zirconium); manufacture and fabrication of special alloys	Local exhaust ventilation; personal protective equipment
Use as control rods in water-cooled nuclear reactors; use in gas-filled tubes and incandescent lamps as scavenger for oxygen and nitrogen; use in the manufacture of photographic flash bulbs, light bulb filaments, and in electronic equipment as cathodes and capacitors	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid proce-

dures and send for first aid or medical assistance.

• **Eye Exposure**

If hafnium, hafnium tetrachloride, or hafnium oxychloride 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 hafnium gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If hafnium tetrachloride or hafnium oxychloride get on the skin, promptly flush the contaminated skin with water. If hafnium or its compounds soak 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 hafnium, hafnium tetrachloride, or hafnium oxychloride, 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 hafnium, hafnium tetrachloride, or hafnium oxychloride 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 hafnium, hafnium tetrachloride, or hafnium oxychloride 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 hafnium, hafnium tetrachloride, or hafnium oxychloride should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Hafnium, hafnium tetrachloride, or hafnium oxychloride may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Hafnium," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR HAFNIUM AND COMPOUNDS (AS HAFNIUM)

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 respirator or quarter mask. 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 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.

Occupational Health Guideline for Heptachlor *

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: $C_{10}H_5Cl_7$ (principal ingredient)
- Synonyms: 1,4,5,6,7,8,8a-Heptachloro-3a,4,7,7a-tetra-hydro-4, 7-methanoindene (principal ingredient)
- Appearance and odor: Light tan, waxy solid with an odor like camphor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for heptachlor is 0.5 milligram of heptachlor per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Heptachlor 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**

In animals, exposure to heptachlor has produced tremors, convulsions, and liver damage. Heptachlor is very similar to chlordane. Exposure to chlordane has caused convulsions and kidney damage in humans.

- **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 heptachlor.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to heptachlor 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 eyes, nervous system, liver, and kidneys should be stressed.

2. Periodic Medical Examination: The aforementioned medical examination should be repeated on an annual basis.

- **Summary of toxicology**

Heptachlor dust is a convulsant in animals. In rats the oral LD50 was 90 mg/kg; within 30 to 60 minutes after administration there were tremors and convulsions; liver damage occurred. Multiple applications of a solution to the skin of rats of 20 mg/kg were toxic, indicating a marked cumulative action. The carcinogenicity of heptachlor was tested in rats by oral administration; one of five experiments suggested hepatocarcinogenicity, but this was not reproduced in the other experiments within the same dose range. Rats given heptachlor in the diet at 6 mg/kg body weight developed cataracts after 4.5 to 9.5 months of feeding. In animals, heptachlor is more potent than chlordane, to which it is closely related chemically; ingestion of chlordane has caused convulsions and kidney damage in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 373.5 (principal ingredient)
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of heptachlor): Not applicable
5. Melting point: 46 – 74 C (114 – 165 F)
6. Vapor pressure at 20 C (68 F): 0.0003 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: Solid: None. Liquid (above 74 C (165 F): Can react with iron and rust to form toxic hydrogen chloride gas.

2. Incompatibilities: Contact of melted heptachlor with iron and rust may form hydrogen chloride gas.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released when heptachlor decomposes.

4. Special precautions: None.

• **Flammability**

1. Not combustible, but may be dissolved in flammable liquid

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of heptachlor.

2. Eye Irritation Level: Heptachlor is not known to be an eye irritant.

3. Evaluation of Warning Properties: Since there is no quantitative information available relating warning properties to air concentrations of heptachlor, it has been treated as a material with poor warning properties. Its concentration in saturated air at 20 C could result in a significant exposure relative to the permissible 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**

An analytical method for heptachlor 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 heptachlor or liquids containing heptachlor where skin contact may occur.

• If employees' clothing has had any possibility of being contaminated with heptachlor or liquids containing heptachlor, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with heptachlor should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of heptachlor from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the heptachlor, the person performing the operation should be informed of heptachlor's hazardous properties.

• Where exposure of an employee's body to heptachlor or liquids containing heptachlor 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 heptachlor should be removed immediately and not reworn until the heptachlor is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where heptachlor or liquids containing heptachlor may contact the eyes.

SANITATION

• Skin that becomes contaminated with heptachlor should be immediately washed or showered with soap or mild detergent and water to remove any heptachlor.

• Workers subject to skin contact with heptachlor or liquids containing heptachlor should wash with soap or mild detergent and water any areas of the body which may have contacted heptachlor at the end of each work day.

• Eating and smoking should not be permitted in areas where heptachlor or liquids containing heptachlor are handled, processed, or stored.

• Employees who handle heptachlor or liquids contain-

ing heptachlor 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 heptachlor may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of pesticides supplied as an emulsifiable concentrate, wettable powder, dust or granular material	Local exhaust ventilation; personal protective equipment; general dilution ventilation
Use as an insecticide in seed treatment, preplanting soil application, dipping tops of plants and roots for control of insects, flies and mosquitoes; use on household plots and on agricultural crops and fruits; use in termite control (dispensed in caulking guns)	Personal protective equipment
Manufacture of heptachlor	*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 heptachlor or liquids containing heptachlor 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 heptachlor or liquids containing heptachlor get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If heptachlor or liquids containing heptachlor soak 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 heptachlor, 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 heptachlor or liquids containing heptachlor 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 heptachlor 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 heptachlor should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Heptachlor 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 this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man,* Volume 5, 1974.

RESPIRATORY PROTECTION FOR HEPTACHLOR

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
5mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m³ or less	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.
700 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 700 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 heptachlor; 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 700 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Heptane

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: $CH_3(CH_2)_5CH_3$
- Synonyms: Normal heptane
- Appearance and odor: Colorless liquid with a mild, gasoline-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for heptane is 500 parts of heptane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2000 milligrams of heptane per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 85 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 440 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Alkanes should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Heptane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to heptane may cause a slight irritation of the eyes, nose, and throat, lightheadedness, hilarity, semi-consciousness, and dizziness. It may also cause loss of appetite and nausea. Higher concentrations may cause unconsciousness.

2. Long-term Exposure: Prolonged overexposure to the liquid 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 heptane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to heptane 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems and the skin should be stressed.

—Skin disease: Heptane is a skin 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.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of heptane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Although heptane 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 heptane 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.

2. Periodic Medical Examination: The aforementioned examinations should be performed on an annual basis.

- **Summary of toxicology**

Heptane vapor is a narcotic. Concentrations of 10,000 to 15,000 ppm produced narcosis in mice within 30 to 60 minutes, while 15,000 to 20,000 ppm caused convulsions

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 death. At 48,000 ppm respiratory arrest was produced in mice in 3 to 4 minutes from the start of exposure. Human subjects exposed to 1000 ppm for 6 minutes, or to 2000 ppm for 4 minutes, reported slight vertigo. At 5000 ppm for 4 minutes, there was marked vertigo, inability to walk a straight line, hilarity, and incoordination, but no complaints of eye and upper respiratory tract or mucous membrane irritation. A 15-minute exposure at 5000 ppm produced in some subjects a state of stupor lasting for 30 minutes after exposure. These subjects also reported loss of appetite, slight nausea, and a taste resembling gasoline for several hours after exposure. The liquid is a defatting agent, and prolonged exposure may cause irritation of the skin. Aspiration may cause a chemical pneumonia. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100
2. Boiling point (760 mm Hg): 98.4 C (209 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of heptane): 3.5
5. Melting point: −90.6 C (−132 F)
6. Vapor pressure at 20 C (68 F): 40 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.005
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 heptane.
4. Special precautions: Heptane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −3.9 C (25 F) (closed cup)
2. Autoignition temperature: 215 C (419 F)
3. Flammable limits in air, % by volume: Lower: 1.05; Upper: 6.7
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Summer reports an odor threshold of 220 ppm; May reports 50 and 220 ppm.
2. Eye Irritation Level: Heptane is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of heptane is well below the permissible exposure limit, heptane 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 heptane. 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 heptane 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 heptane may be used. A analytical method for heptane 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 heptane.
- Any clothing which becomes wet with liquid heptane should be removed immediately and not reworn until the heptane is removed from the clothing.
- Clothing wet with liquid heptane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of heptane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the heptane, the person performing the operation should be informed of heptane's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid heptane may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to heptane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid heptane should be promptly washed or showered with soap or mild detergent and water to remove any heptane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to heptane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a carrier and penetrant solvent for adhesives, use in azeotrophic distillations, and in rubber tire manufacture; as a solvent in rubber cements	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an ink solvent in gravure printing	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent in polymer industry as a swelling and blowing agent for plastic foams	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a reference fuel for testing gasoline engine knock and pollution and combustion studies	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a diluent solvent for lacquers during preparation and application	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic chemical synthesis in preparations of toluene and alkylbenzenes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an extraction solvent for tallow from meat, rosin from wood, and oils from seeds	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in cleaning surfaces before application of adhesives	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a laboratory solvent for scientific testing	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 heptane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If heptane gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If heptane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of heptane, 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 heptane 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 heptane 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. Heptane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Heptane may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR HEPTANE

Condition	*Minimum Respiratory Protection** Required Above 500 ppm
Vapor Concentration	
850 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
4250 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 4250 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 Hexachloroethane*

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: CCl_3CCl_3
- *Synonyms:* Perchloroethane
- Appearance and odor: Colorless solid with a camphor-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hexachloroethane is 1 part of hexachloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 10 milligrams of hexachloroethane per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of their recommended Threshold Limit Value for hexachloroethane from 1 ppm to 10 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hexachloroethane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may be absorbed through the skin.

- **Effects of overexposure**

Exposure to the hot fumes of hexachloroethane may cause 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 hexachloroethane. employee who is exposed to hexachloroethane at potentially hazardous levels.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to hexachloroethane at potentially hazardous levels.

- **Summary of toxicology**

Hexachloroethane is an eye irritant. High oral doses in animals cause hepatic, renal, and central nervous system effects. Dogs given oral doses of 1 to 1.4 g/kg showed depression of the central nervous system characterized by weakness, staggering, and muscle twitching. When administered orally to domestic animals as a parasiticide, it caused chronic lesions in the liver and acute, diffuse nephrosis in cattle at high doses, but it had no noticeable toxic effect in horses at levels of 0.2 g/kg. Exposure of workmen to fumes from hot hexachloroethane resulted in blepharospasm, photophobia, lacrimation, and reddening of the conjunctiva, but no corneal injury or permanent damage. No chronic effects have been reported from industrial exposure, although significant absorption through the skin is said to occur.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 236.7
2. Boiling point (760 mm Hg): 189 C (372 F) (sublimes)
3. Specific gravity (water = 1): 2.1
4. Vapor density (air = 1 at boiling point of hexachloroethane): 8.2
5. Melting point: 189 C (372 F) (sealed tube)
6. Vapor pressure at 20 C (68 F): 0.22 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.005
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

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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1. Conditions contributing to instability: Heat

2. Incompatibilities: Hexachloroethane reacts with hot iron, zinc, and aluminum. Dehalogenation by reaction with alkalies will produce spontaneously explosive chloroacetylene.

3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, chlorine, carbon tetrachloride, and tetrachloroethylene) may be released when hexachloroethane decomposes.

4. Special precautions: Liquid hexachloroethane will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Although hexachloroethane has a camphor-like odor, no quantitative data are available relating air concentrations of this substance to 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 hexachloroethane 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 hexachloroethane may be used. An analytical method for hexachloroethane 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 hexachloroethane or liquids containing hexachloroethane.

• If employees' clothing may have become contaminated with solid hexachloroethane or liquids containing hexachloroethane, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with solid hexachloroethane or liquids containing hexachloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hexachloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hexachloroethane, the person performing the operation should be informed of hexachloroethane's hazardous properties.

• Non-impervious clothing which becomes contaminated with solid hexachloroethane or liquids containing hexachloroethane should be removed promptly and not reworn until the hexachloroethane is removed from the clothing.

SANITATION

• Workers subject to skin contact with solid hexachloroethane or liquids containing hexachloroethane should wash with soap or mild detergent and water any areas of the body which may have contacted hexachloroethane at the end of each work day.

• Skin that becomes contaminated with solid hexachloroethane or liquids containing hexachloroethane should be promptly washed or showered with soap or mild detergent and water to remove any hexachloroethane.

• Employees who handle solid hexachloroethane or liquids containing hexachloroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

• Eating and smoking should not be permitted in areas where solid hexachloroethane or liquids containing hexachloroethane are handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hexachloroethane may occur and

control methods which may be effective in each case:

Operation	Controls
Use in manufacture of pyrotechnics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in lubricants in foundries for mold treatment; extreme-pressure lubricants; use in preparation of nitrocellulose esters camphor substitutes; use as a fumigant, insecticide, fungicide, and animal antihelmintics; use as a modifier in manufacture of synthetic rubber	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a chemical additive; use to reduce ignitability of combustibles, and as submarine paint to prevent corrosion; as an additive to fire extinguishers	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 hexachloroethane 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 hexachloroethane gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquids containing hexachloroethane soak through the clothing, remove the clothing immediately 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 hexachloroethane, 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 immediately.

• **Swallowing**

When hexachloroethane 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 hexachloroethane is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing hexachloroethane should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Hexachloroethane may be disposed of 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 HEXACHLOROETHANE

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.
300 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 300 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 pesticide respirator providing protection against pesticides. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Hexachloronaphthalene (Halowax 1014)

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: $C_{10}H_2Cl_6$
- Synonyms: Halowax 1014
- Appearance and odor: Light yellow solid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Halowax 1014 is 0.2 milligram of Halowax 1014 per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Halowax 1014 can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Overexposure to Halowax 1014 may cause an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, yellow jaundice, and possibly 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 Halowax 1014.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Halowax 1014 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: Since this substance is a known liver toxin, a profile of liver function should be obtained by using 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**

Halowax 1014 vapor and dust are toxic to the liver and the skin. Repeated exposure to an average concentration of 8.9 mg/m^3 of a mixture of penta- and Halowax 1014 produced jaundice and was fatal to rats; the liver showed marked fatty degeneration and centrolobular necrosis. At concentrations of mixed penta- and Halowax 1014 averaging 1 to 2 mg/m^3, there were human fatalities due to acute yellow atrophy of the liver. Such exposures produced jaundice associated with nausea, indigestion, and weight loss. The acute late stage progresses from restlessness to confusion, fever, and coma. Exposure of workers by inhalation of vapor or dust, or by skin absorption, has caused a severe acneform dermatitis termed chloracne, as well as serious liver injury.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 335
2. Boiling point (760 mm Hg): 343 to 388 C (650 to 730 F) (approximately)
3. Specific gravity (water = 1): 1.78
4. Vapor density (air = 1 at boiling point of Halowax 1014): 11.6
5. Melting point: 137 C (279 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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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): Much less than 1

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Halowax 1014 reacts with strong oxidizing agents.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released when Halowax 1014 decomposes.

4. Special precautions: None

• **Flammability**

1. Not combustible

• **Warning properties**

No quantitative data are available on the relationship between air concentrations of the chloronaphthalenes and warning properties. Vapor pressure at 20 C is less than 1 mm Hg, creating a concentration of less than 1500 ppm at 20 C.

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 Halowax 1014 on a filter, followed by extraction with hexane, and gas chromatographic analysis. An analytical method for Halowax 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 molten Halowax 1014.

• 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 Halowax 1014 or with liquids containing Halowax 1014.

• 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 Halowax 1014 fumes from the heated material.

• Non-impervious clothing which becomes contaminated with molten Halowax 1014 should be removed immediately and not reworn until the Halowax 1014 is removed from the clothing.

• Non-impervious clothing which becomes contaminated with solid Halowax 1014 or liquids containing Halowax 1014 should be removed promptly and not reworn until the Halowax 1014 is removed from the clothing.

• If employees' clothing may have become contaminated with solid Halowax 1014, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with Halowax 1014 should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of Halowax 1014 from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the Halowax 1014, the person performing the operation should be informed of Halowax 1014's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten Halowax 1014 contacting the eyes.

• Employees should be provided with and required to use splash-proof safety goggles where solid Halowax 1014 or liquids containing Halowax 1014 may contact the eyes.

SANITATION

• Eating and smoking should not be permitted in areas where Halowax 1014 is handled, processed, or stored.

• Workers subject to skin contact with Halowax 1014 should wash with soap or mild detergent and water any areas of the body which may have contacted Halowax 1014 at the end of each work day.
• Skin that becomes contaminated with solid Halowax 1014 or liquids containing Halowax 1014 should be promptly washed or showered with soap or mild detergent and water to remove any Halowax 1014.
• Employees who handle Halowax 1014 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 Halowax 1014 may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture (pouring, dipping, and peeling) of electric equipment as insulating material	Local exhaust ventilation; personal protective equipment; general dilution ventilation with intake and exhaust fans
Use as an inert component of resins or polymers for coating or impregnating textiles, wood, paper for flame- and water-proofing, and fungicidal and insecticidal properties	Process enclosure; local exhaust ventilation with intake and exhaust fans; general dilution ventilation
Use as an additive to special lubricants	General dilution ventilation
Use as an additive to cutting oils and special lubricants	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use of electrical equipment when substance used as insulating material	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in polymer manufacture as fillers; use during manufacture of special lubricants	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 solid Halowax 1014 or liquids containing Halowax 1014 get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. If molten Halowax 1014 gets into the eyes, immediately flush the eyes with large amounts of water to remove the heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.
• **Skin Exposure**
If non-impervious clothing becomes soiled with Halowax 1014, remove and clean the clothing before wearing again. If non-impervious clothing becomes heavily contaminated, it should be destroyed. If solid Halowax 1014 or liquids containing Halowax 1014 get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If skin irritation persists after washing, get medical attention. If molten Halowax 1014 gets on the skin or non-impervious clothing, immediately flush the affected area with large amounts of water to remove heat. Get medical attention immediately.
• **Breathing**
If a person breathes in large amounts of Halowax 1014, 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 immediately.
• **Swallowing**
When Halowax 1014 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 Halowax 1014 is spilled, the following steps should be taken:
1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing Halowax 1014

should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Halowax 1014 may be disposed of in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Hexachloronaphthalene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR HALOWAX 1014

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m³
Particulate or Vapor Concentration	
2 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 2 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.

Occupational Health Guideline for Hexane

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: $CH_3(CH_2)_4CH_3$
- Synonyms: Hexyl hydride; normal hexane
- Appearance and odor: Colorless liquid with a mild, gasoline-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hexane is 500 parts of hexane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1800 milligrams of hexane per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 100 ppm (350 mg/m³) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 510 ppm (1,800 mg/m³) averaged over a 15-minute period. The NIOSH Criteria Document for Alkanes should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hexane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to hexane may cause lightheadedness, giddiness, nausea, and headache. It may also cause irritation of the eyes and nose. Greater exposure may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure to the liquid 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 hexane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hexane 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems and the skin should be stressed.

—Skin disease: Hexane 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.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of hexane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Although hexane 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 hexane 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.

2. Periodic Medical Examination: The aforementioned examinations should be performed on an annual basis.

- **Summary of toxicology**

Hexane vapor is a narcotic; it also is a mild upper respiratory irritant. Polyneuropathy has been reported to occur in Japanese workers exposed to hexane vapors. Effects appeared to be reversible. Concentrations of 30,000 ppm produced narcosis in mice within 30 to 60

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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minutes; convulsions and death occurred at 35,000 to 40,000 ppm; at 64,000 ppm respiratory arrest was produced in 2.5 to 4.5 minutes from the start of exposure. Concentrations up to 8000 ppm produced no anesthesia. In human subjects, 2000 ppm for 10 minutes produced no effects, but 5000 ppm resulted in dizziness and a sensation of giddiness. Other investigators reported slight nausea, headache, and irritation of the eyes and throat at 1400 to 1500 ppm. In industrial practice, mild narcotic symptoms such as dizziness have been observed when concentrations exceeded 1000 ppm, but not below 500 ppm. Chronic effects have rarely been reported. The liquid is a defatting agent, and prolonged exposure may cause irritation of the skin. Aspiration may cause a chemical pneumonia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 86
  2. Boiling point (760 mm Hg): 68.9 C (156 F)
  3. Specific gravity (water = 1): 0.7
  4. Vapor density (air = 1 at boiling point of hexane): 3.0
  5. Melting point: −95 C (−139 F)
  6. Vapor pressure at 20 C (68 F): 124 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.014
  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 hexane.
  4. Special precautions: Hexane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −21.7 C (−7 F) (closed cup)
  2. Autoignition temperature: 225 C (437 F)
  3. Flammable limits in air, % by volume: Lower: 1.1; Upper: 7.5
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: No quantitative information is available.
  2. Irritation Levels: The *Documentation of TLV's* notes that "Drinker, Yaglou, and Warren found slight nausea, headache, and eye and throat irritation at 1400 to 1500 ppm. Nelson found no irritation at 500 ppm in unacclimated subjects."
  3. Evaluation of Warning Properties: Since hexane can be detected at a concentration approximately 3 times 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 hexane. 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 hexane 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 hexane may be used. An analytical method for hexane 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 hexane.
- Any clothing which becomes wet with liquid hexane should be removed immediately and not reworn until the hexane is removed from the clothing.
- Clothing wet with liquid hexane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hexane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hexane, the person performing the operation should be informed of hexane's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid hexane may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to hexane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid hexane should be promptly washed or showered with soap or mild detergent and water to remove any hexane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hexane may occur and control methods which may be effective in each case:

Operation	Controls
Use as an extractant of agricultural products	Process enclosure; general dilution ventilation
Use in manufacture of polyolefins and certain elastomers as a catalyst carrier and assist in controlling molecular weight by dropping polymer out of solution when a certain molecular weight is reached	Process enclosure; general dilution ventilation; personal protective equipment
Use as an extractant of animal fat	Process enclosure; general dilution ventilation; personal protective equipment
Use as a solvent in adhesives to control viscosity and reduce drying time	General dilution ventilation; personal protective equipment
Use in pharmaceutical industry as a reaction medium, immiscible solvent, and extraction ergot	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during compounding of adhesives as a diluent or vehicle solvent; use in compounding printing inks, lacquers, or stains; use as a laboratory reagent and general solvent; use in manufacture of low-temperature thermometers	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 hexane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If hexane gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If hexane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of hexane, 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 hexane 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 hexane 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. Hexane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Hexane may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR HEXANE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). 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. Any supplied-air respirator with a full facepiece, helmet, or hood. *Any self-contained breathing apparatus with a full facepiece.*
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 2-HEXANONE

INTRODUCTION

This guideline summarizes pertinent information about 2-hexanone 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:** $C_6H_{12}O$
- **Structure:**

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_3$$

- **Synonyms:** Butyl methyl ketone, MBK, methyl butyl ketone, methyl n-butyl ketone
- **Identifiers:** CAS 591-78-6; RTECS MP1400000; DOT not assigned
- **Appearance and odor:** Colorless liquid with an odor like acetone but more pungent

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100.18
2. Boiling point (at 760 mmHg): 127.8°C (262°F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of 2-hexanone): 3.5
5. Melting point: -57°C (-71°F)
6. Vapor pressure at 20°C (68°F): 3.0 mmHg; at 25°C (77°F), 3.8 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 1.4
8. Evaporation rate (butyl acetate = 1): Approximately 1
9. Saturation concentration in air (approximate) at 20°C (68°F): 0.4% (4,000 ppm); at 25°C (77°F), 0.5% (5,000 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving 2-hexanone.
3. Caution: 2-Hexanone will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 25°C (77°F) (closed cup)
2. Autoignition temperature: 425°C (795°F)
3. Flammable limits in air, % by volume: Lower, 1.2; upper, 8
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 0.076 ppm
2. Eye irritation levels: 1,000 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, 2-hexanone can be detected below the National Institute for Safety and Health (NIOSH) recommended exposure limit (REL); thus, 2-hexanone 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-hexanone is 100 parts of 2-hexanone per million parts of air (ppm) [410 milligrams of 2-hexanone 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 (4 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 5 ppm (20 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for 2-hexanone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	100	410
NIOSH REL TWA	1	4
ACGIH TLV® TWA	5	20

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HEALTH HAZARD INFORMATION

• **Routes of exposure**

2-Hexanone 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 2-hexanone by guinea pigs caused central nervous system depression, narcosis, coma, and death. Subchronic inhalation of 2-hexanone by rats, cats, dogs, chickens, and monkeys produced peripheral neuropathy, characterized by paralysis, nerve swelling, and loss of nerve sheath covering.

2. *Effects on humans:* Chronic inhalation or dermal exposure of workers has caused peripheral neuropathy.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 2-hexanone can cause headaches, drowsiness, and unconsciousness. Moderate irritation of the eyes, nose, and throat can also occur.

2. *Long-term (chronic):* Exposure to 2-hexanone can cause lightheadedness, weight loss, fatigue, intermittent tingling or prickling sensations in the arms or legs, and progressive weakness of the limbs. Dryness, irritation, and inflammation of the 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 2-hexanone, 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-hexanone 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 chronic concurrent dermatitis, or a history and physical findings consistent with peripheral neuropathy. In addition to the medical interview and physical examination, the means to identify these conditions may include electromyography of the extremities using standardized methods and evaluation criteria.

• **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-hexanone. 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 respiratory and 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 2-hexanone may cause peripheral neuropathy after a prolonged period of 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: Inflammatory and toxic neuropathy.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to 2-hexanone 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 2-hexanone 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 2-hexanone may also be used if available. A detailed sampling and analytical method for 2-hexanone 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 2-hexanone.

Workers should be provided with and required to use splash-proof safety goggles where 2-hexanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with 2-hexanone 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-hexanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-hexanone'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-hexanone 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 use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 2-hexanone 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-hexanone 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-hexanone

Operations	Controls
During use as a commercial solvent for nitrocellulose, natural and synthetic resins, oils, waxes, vinyl polymers and copolymers, and cellulose acetates	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a solvent in the manufacture of varnish removers, vinyl lacquers, and nitrate wood lacquers	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as an extractive solvent for paraffin wax; during use in the separation and purification of certain metals	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 2-hexanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-hexanone 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-hexanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-hexanone gets on the skin, wash it immediately with soap and water. If 2-hexanone 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-hexanone 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-hexanone, 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-hexanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing 2-hexanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. 2-Hexanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing 2-hexanone 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-hexanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 10 ppm	Any supplied-air respirator
	Any self-contained breathing apparatus
Less than or equal to 25 ppm	Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 50 ppm	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 operated in a continuous flow mode
Less than or equal to 1,000 ppm	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Less than or equal to 2,000 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 2,000 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 1 ppm (4 mg/m^3) (TWA).

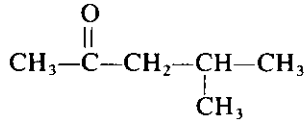
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR HEXONE

INTRODUCTION

This guideline summarizes pertinent information about hexone 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:** $C_6H_{12}O$
- **Structure:**



- **Synonyms:** Isobutyl methyl ketone; isopropylacetone; methyl isobutyl ketone; 4-methyl-2-pentanone; MIBK
- **Identifiers:** CAS 108-10-1; RTECS SA9275000; DOT 1245, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a sweet, pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100.18
2. Boiling point (at 760 mmHg): 118°C (244°F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of hexone): 3.5
5. Melting point: -84°C (-119°F)
6. Vapor pressure at 25°C (77°F): 7.5 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 1.9
8. Evaporation rate (butyl acetate = 1): 1.64
9. Saturation concentration in air (approximate) at 25°C (77°F): 1.0% (10,000 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving hexone.
3. Caution: Hexone will dissolve some plastics, resins, and rubber.

- **Flammability**

1. Flash point: 18°C (64°F) (closed cup)
2. Autoignition temperature: 460°C (860°F)
3. Flammable limits in air, % by volume: Lower, 1.4; upper, 7.5
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: 0.68 ppm
2. Eye irritation level: 200-400 ppm
3. Nose and throat irritation may occur at 400 ppm.
4. Evaluation of warning properties for respirator selection: Because of its odor, hexone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, hexone is treated as a chemical with adequate warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for hexone is 100 parts of hexone per million parts of air (ppm) [410 milligrams of hexone per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 50 ppm (200 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 50 ppm (205 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek; and the ACGIH short-term exposure limit (STEL) is 75 ppm (300 mg/m^3) (Table 1).

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Table 1.—Occupational exposure limits for hexone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	100	410
NIOSH REL TWA	50	200
ACGIH TLV® TWA	50	205
STEL	75	300

HEALTH HAZARD INFORMATION

• **Routes of exposure**

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

• **Summary of toxicology**

1. *Effects on animals:* Subchronic inhalation of hexone by rats produced degeneration and necrosis of kidney tubules and increased kidney and liver weights.

2. *Effects on humans:* Inhalation exposure of workers to hexone has produced narcosis and slight liver enlargement.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to hexone can cause nausea, vomiting, headaches, weakness, dizziness, incoordination, and drowsiness. Irritation of the eyes, nose, throat, and respiratory tract can also occur.

2. *Long-term (chronic):* Exposure to hexone 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 hexone, 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 reproductive, 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 hexone 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 hexone. 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 hexone 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 hexone 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 hexone may also be used if available. A detailed sampling and analytical method for hexone 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 hexone.

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

SANITATION

Clothing which is contaminated with hexone 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 hexone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of hexone's hazardous properties.

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

Skin that becomes contaminated with hexone 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 use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle hexone 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 hexone 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 hexone

Operations	Controls
During application and drying of lacquers, varnishes, epoxy, acrylic, vinyl, or other cellulose- or resin-based coatings, finishes, and adhesives	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a separating agent for certain inorganic salts	General dilution ventilation
During extraction in the manufacture of antibiotics and purification of petroleum products (dewaxing)	General dilution ventilation
During the manufacture of dry cleaning preparations, germicides, fungicides, and electroplating solutions	General dilution ventilation
During use in blending raw materials for molded plastics	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use in cleaning and maintaining ketone processing equipment	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 hexone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If hexone 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 hexone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If hexone gets on the skin, wash it immediately with soap and water. If hexone 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 hexone 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 hexone, 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 hexone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing hexone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Hexone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing hexone 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 hexone

Condition	Minimum Respiratory Protection*†
Concentration:	
Less than or equal to 500 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	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)
Less than or equal to 1,000 ppm	Any powered air-purifying respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	Any chemical cartridge respirator with a full facepiece and organic vapor cartridge(s)
Less than or equal to 1,250 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 2,500 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
	Any supplied air respirator with a tight-fitting facepiece operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 3,000 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 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 50 ppm 200 mg/m^3) (TWA).

Occupational Health Guideline for sec-Hexyl Acetate

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: $CH_3COOCH(CH_3)CH_2CH(CH_3)_2$
- Synonyms: 1,3-Dimethylbutyl acetate; methylamyl acetate; methylisoamyl acetate; methylisobutyl carbinol acetate; hexyl acetate
- Appearance and odor: Colorless liquid with a mild, pleasant, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sec-hexyl acetate is 50 parts of sec-hexyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 300 milligrams of sec-hexyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

sec-Hexyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- ***Effects of overexposure***

1. Short-term Exposure: Overexposure to sec-hexyl acetate may cause eye and throat irritation. It may also cause headache, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged exposure to sec-hexyl acetate 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 sec-hexyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sec-hexyl acetate 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 sec-hexyl acetate exposure.

—Kidney disease: Although sec-hexyl acetate 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 sec-hexyl acetate might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although sec-hexyl acetate 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: sec-Hexyl acetate 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**

High concentrations of sec-hexyl acetate vapor may be mildly irritating to the eyes and upper respiratory tract. The lethal dose for animals by inhalation is approximately 4000 ppm, although rats survived 8 hour exposures to concentrated vapors. This agent is poorly absorbed through the skin. 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.

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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

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 144
  2. Boiling point (760 mm Hg): 141 C (285 F)
  3. Specific gravity (water = 1): 0.86
  4. Vapor density (air = 1 at boiling point of sec-hexyl acetate): 5.0
  5. Melting point: −64 C (−83 F)
  6. Vapor pressure at 20 C (68 F): 4 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.13
  8. Evaporation rate (butyl acetate = 1): 0.47
- **Reactivity**
  1. Conditions contributing to instability: Heat
  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 sec-hexyl acetate.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 45 C (113 F) (closed cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: 0.9 (calculated at flash point)
  4. Extinguishant: Dry chemical, foam, or carbon dioxide
- **Warning properties**
  1. Odor Threshold: The *Documentation of TLV's* reports that human subjects noted an unpleasant odor at 100 ppm.
  2. Eye Irritation Level: The *Documentation of TLV's* also reports that eye irritation was experienced by human subjects exposed to 100 ppm. The TLV was recommended "to prevent significant eye irritation."
  3. Other Information: According to the *Documentation of TLV's*, the human subject noted an unpleasant taste at 100 ppm.
  4. Evaluation of Warning Properties: At a concentration of only twice the permissible exposure limit, human subjects can detect sec-hexyl acetate through odor, eye irritation, and taste. 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 sec-hexyl acetate 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 sec-hexyl acetate may be used. An analytical method for sec-hexyl acetate 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 sec-hexyl acetate.
- Clothing wet with liquid sec-hexyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sec-hexyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sec-hexyl acetate, the person performing the operation should be informed of sec-hexyl acetate's hazardous properties.
- Non-impervious clothing which becomes wet with sec-hexyl acetate should be removed promptly and not reworn until the sec-hexyl acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid sec-hexyl acetate may contact the eyes.

SANITATION

• Skin that becomes wet with liquid sec-hexyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any sec-hexyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sec-hexyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Use during application of nitrocellulose lacquers and other lacquers	General dilution ventilation; local exhaust ventilation
Liberation during manufacture of nitrocellulose and other lacquers	General dilution ventilation
Liberation during use as an inhibitor in handling of diacyl peroxide solutions	Process enclosure; 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 sec-hexyl acetate 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 sec-hexyl acetate gets on the skin, promptly flush the contaminated skin with water. If sec-hexyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of sec-hexyl acetate, 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 sec-hexyl acetate 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 sec-hexyl acetate 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. Liquid sec-hexyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

sec-Hexyl acetate 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.

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RESPIRATORY PROTECTION FOR SEC-HEXYL ACETATE

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).
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.
4000 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 4000 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 HYDRAZINE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about hydrazine 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:** N_2H_4
- **Structure:** $H_2N\text{-}NH_2$
- **Synonyms:** Diamide, diamine, hydrazine base, hydrazine anhydrous
- **Identifiers:** CAS 302-01-2; RTECS MU7175000; DOT 2029, label required: "Flammable Liquid and Poison"
- **Appearance and odor:** Colorless oily liquid that fumes in air and has a fishy or ammonia-like odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 32.06
2. Boiling point (at 760 mmHg): 113.5°C (236°F)
3. Specific gravity (water = 1): 1.004
4. Vapor density (air = 1 at boiling point of hydrazine): 1.04
5. Melting point: 1.4°C (34°F)
6. Vapor pressure at 25°C (77°F): 14.4 mmHg
7. Miscible with water
8. Evaporation rate (butyl acetate = 1): 0.42
9. Saturation concentration in air (approximate) at 25°C (77°F): 1.89% (18,900 ppm)
10. Ionization potential: 8.36 eV

- **Reactivity**

1. Incompatibilities: Hydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving hydrazine.
3. Caution: Hydrazine will attack cork and some forms of plastic, coatings, and rubber.

- **Flammability**

1. Flash point: 37.7°C (100°F) (closed cup)
2. Autoignition temperature: 24°C (75.2°F) on iron rust surface, 270°C (518°F) on glass surface
3. Flammable limits in air, % by volume: Lower, 4.7; Upper, 98
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Caution: Hydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

Odor threshold: 3-4 ppm

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 hydrazine is 1.0 part of hydrazine per million parts of air (ppm) [1.3 milligrams of hydrazine 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 the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that hydrazine 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 0.03 ppm (0.04 mg/m^3) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the

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Division of Standards Development and Technology Transfer

lowest concentration reliably detectable by current NIOSH-validated sampling and analytical methods. The American Conference of Governmental Industrial Hygienist (ACGIH) has designated hydrazine as an A2 substance (suspected human carcinogen) having as assigned threshold limit value (TLV®) of 0.1 ppm (0.1 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for hydrazine

	Exposure limits ppm	mg/m³
OSHA PEL TWA (Skin)*	1.0	1.3
NIOSH REL (Ca)†		
Ceiling (120 min)	0.03	0.04
ACGIH TLV® (A2)§		
TWA (Skin)	0.1	0.1

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

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

• Summary of toxicology

1. *Effects on animals:* Acute exposure of multiple species of animals to hydrazine by several routes of administration caused loss of appetite and weight, lethargy, vomiting, significant irritation of eyes, skin, and mucous membranes, hemolysis, fatty degeneration and lipid deposition in the liver and kidneys, and central nervous system (CNS) effects manifested by convulsions and death. Subchronic or chronic exposure of mice and rats to hydrazine by several routes of administration produced cancers of the liver, lung, or lymph tissues.

2. *Effects on humans:* A worker exposed to hydrazine hydrate once a week for six months developed fluid in the chest cavity, pulmonary edema, bronchitis, enlarged liver and kidneys, tissue destruction (necrosis) of the liver, intestinal hemorrhage, and death.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to hydrazine can cause dizziness, nausea, skin burns, and irritation of the eyes, nose, and throat.

2. *Long-term (chronic):* Exposure to hydrazine can cause lethargy, vomiting, tremors, itching and burning of the eyes and skin, conjunctivitis, and contact 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 hydrazine, 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 hematopoietic (blood-cell forming), 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). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

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 hydrazine 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. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to hydrazine.

• **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 hydrazine. 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 eyes, skin, liver, kidneys, and hematopoietic, 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 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 hydrazine 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 hydrazine. 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 120-minute sample or a series of consecutive samples that total 120 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 hydrazine vapors with hydrochloric acid-filled midget bubblers and analyzing by visible absorption spectrophotometry. Direct-reading devices calibrated to measure hydrazine may also be used if available. A detailed sampling and analytical method for hydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 3503).

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 hydrazine.

SANITATION

Clothing which is contaminated with hydrazine 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 hydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of hydrazine'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 hydrazine 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 use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle hydrazine 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 hydrazine 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 hydrazine

Operations	Controls
During use in the synthesis and handling of high-energy fuels, agricultural chemicals, pharmaceuticals, chemicals for plastics and rubber manufacturing, textile agents and dye intermediates, and photographic chemicals	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an anticorrosion agent; during use in the application of metal coatings on nonconducting materials	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 hydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If hydrazine 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 hydrazine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If hydrazine gets on the skin, wash it immediately with soap and water. If hydrazine 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 hydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing hydrazine may be flushed with water and collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing hydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Hydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

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 hydrazine

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 appropriate escape-type self-contained breathing apparatus

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

Occupational Health Guideline for Hydrogen Bromide

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: HBr
- Synonyms: Anhydrous hydrobromic acid
- Appearance and odor: Colorless gas with an irritating, sharp odor. It also can be a liquid when stored under pressure.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen bromide is 3 parts of hydrogen bromide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 10 milligrams of hydrogen bromide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen bromide 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: Hydrogen bromide may cause irritation of the eyes, nose, and throat. If a solution is splashed on the skin or in the eyes, it will cause a burn.

2. Long-term Exposure: Repeated or prolonged exposure to hydrogen bromide may cause irritation of the nose and throat with mucous production and indigestion.

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 hydrogen bromide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen bromide 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 hydrogen bromide exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of hydrogen bromide might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Hydrogen bromide is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Hydrogen bromide is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems 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**

Hydrogen bromide gas irritates the eyes, mucous membranes, and skin. Experimental exposure of humans to 5 ppm for several minutes caused nose and throat irritation in most individuals, and a few were affected at concentrations of 3 to 4 ppm. Solutions and the vapor irritate the upper respiratory tract. Contact with the eyes, skin, or mucous membranes may cause burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 80.92
  2. Boiling point (760 mm Hg): −66.8 C (−88.2 F)
  3. Specific gravity (water = 1): 2.16
  4. Vapor density (air = 1 at boiling point of hydro-

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

gen bromide): 2.8

5. Melting point: −86.9 C (−124 F)

6. Vapor pressure at 16.8 C (62 F): 20 atm.

7. Solubility in water, g/100 g water at 20 C (68 F): 194

8. Evaporation rate (butyl acetate = 1): Not pertinent

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact of liquid hydrogen bromide with strong oxidizers, strong caustics, metals, and moisture may cause violent spattering and fire.

3. Hazardous decomposition products: None

4. Special precautions: In the presence of moisture, hydrogen bromide liquid or gas will attack most metals with the formation of flammable hydrogen gas.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, the odor of hydrogen bromide is detectable at 2 ppm.

2. Eye Irritation Level: According to the *Documentation of TLV's*, no eye irritation was observed in human subjects exposed to concentrations up to 6 ppm. Kirk and Othmer state that hydrogen bromide is an eye irritant, but do not specify the necessary concentration.

3. Other Information: The *Documentation of TLV's* reports that 1 out of 6 human subjects experienced nose and throat irritation at 3 ppm hydrogen bromide. At 4 ppm, 3 out of 6 experienced nose irritation. All exposed subjects experienced nose irritation at 5 and 6 ppm. Only 1 out of 6 subjects experienced throat irritation at concentrations of 4 ppm, 5 ppm, and 6 ppm.

4. Evaluation of Warning Properties: Through its odor and irritant effects, hydrogen bromide can be detected at the permissible exposure limit or slightly above it. Therefore, hydrogen bromide 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 hydrogen bromide in a bubbler containing sodium hydroxide, followed by analysis with an ion-specific electrode. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen bromide may be used. An analytical method for hydrogen bromide 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 liquid hydrogen bromide or solutions containing hydrogen bromide.

• Clothing contaminated with hydrogen bromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen bromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen bromide, the person performing the operation should be informed of hydrogen bromide's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid hydrogen bromide or solutions containing hydrogen bromide, 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 hydrogen bromide should be removed immediately and not reworn until the hydrogen bromide 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 hydrogen bromide or solutions containing hydrogen bromide contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid hydrogen bromide or solutions containing hydrogen bromide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with hydrogen bromide should be immediately washed or showered to remove any hydrogen bromide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen bromide may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of inorganic bromides for use in photography, pharmaceuticals, industrial drying, textile finishing, engraving and lithography, chemical synthesis, and fire retardants	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of brominated fluorocarbons for fire extinguishing, refrigeration, and aerosols	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis as intermediates for barbituate manufacture, manufacture of synthetic hormones, catalyst for alkylations, controlled oxidations, isomerizations, and polymerizations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during decomposition of brominated fluorocarbon fire-extinguishing agents or flame-retardant chemicals	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a reagent in analytical chemistry; use in etching of germanium crystals, silicon discs, and metal alloys	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent for ore minerals	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 hydrogen bromide or solutions containing hydrogen bromide 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 hydrogen bromide or solutions containing hydrogen bromide get on the skin, immediately flush the contaminated skin with water. If liquid hydrogen bromide or solutions containing hydrogen bromide penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention promptly.

• **Breathing**

If a person breathes in large amounts of hydrogen bromide, 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 a solution of hydrogen bromide has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the hydrogen bromide. 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 hydrogen bromide is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
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, allow to vaporize and disperse the gas.

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RESPIRATORY PROTECTION FOR HYDROGEN BROMIDE

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Gas or Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with a full facepiece and an acid gas cartridge(s). A gas mask with a chin-style or a front- or back-mounted acid gas canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 50 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 acid gases. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Hydrogen Chloride

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: HCl
- Synonyms: Anhydrous hydrogen chloride; hydrochloric acid, anhydrous
- Appearance and odor: Colorless gas with an irritating, pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen chloride is a ceiling of 5 parts of hydrogen chloride per million parts of air (ppm). This may also be expressed as 7 milligrams of hydrogen chloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen chloride 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: When hydrogen chloride gas is inhaled, it may cause irritation of the respiratory tract with burning, choking, and coughing. Severe breathing difficulties may occur which may be delayed in onset. At times ulceration of the nose and throat may occur. Hydrogen chloride gas and solutions of hydrogen chloride (hydrochloric acid) may cause eye irritation, severe burns, and permanent damage with loss of sight. Solutions of hydrogen chloride may cause severe burns of the skin unless the acid is washed off immediately. Exposure of the skin to hydrogen chloride gas may cause skin inflammation or burns. Swallowing hydrogen chloride solution may cause burns of the mouth, throat, and stomach.

2. Long-term Exposure: Repeated or prolonged exposure to hydrogen chloride may cause erosion of the teeth. Repeated exposure of the skin to dilute solutions of hydrogen chloride 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 hydrogen chloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen chloride 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, skin, and eyes should be stressed.

—14" x 17" chest roentgenogram: Hydrogen chloride causes lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Hydrogen chloride 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 by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Hydrogen chloride gas irritates the eyes, mucous membranes, and skin. Exposure of rabbits and guinea pigs to 6400 mg/m^3 (approximately 4290 ppm) for 30 minutes caused death, in many instances from laryngeal spasm, laryngeal edema, or pulmonary edema. Exposure of three species of animals to 300 ppm for 6 hours caused

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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corneal and upper respiratory irritation. In humans, exposure to the gas immediately causes severe irritation of the upper respiratory tract resulting in cough, burning of the throat, and a choking sensation; effects are usually limited to inflammation and occasionally ulceration of the nose, throat, and larynx; if inhaled deeply, pulmonary edema may occur. In workers, exposure to 50 to 100 ppm for 1 hour was barely tolerable; short exposure to 35 ppm caused irritation of the throat, and 10 ppm was considered the maximal concentration allowable for prolonged exposure. High concentrations of the gas caused eye irritation and may cause prolonged or permanent visual impairment, including total loss of vision. Exposure of the skin to a high concentration of the gas or to a concentrated solution of the gas (hydrochloric acid) will cause burns; repeated or prolonged exposure to dilute solutions may cause dermatitis. Erosion of the teeth may occur from repeated or prolonged exposure. Although unlikely to occur, ingestion of hydrochloric acid causes severe burns of the mucous membranes of the mouth, esophagus, and stomach; pain; nausea and vomiting.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 36.5
2. Boiling point (760 mm Hg): −85 C (−121 F)
3. Specific gravity (water = 1): 1.194 (liquid)
4. Vapor density (air = 1 at boiling point of hydrogen chloride): 1.27
5. Melting point: −114 C (−173 F) (triple point)
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): 62
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: High temperatures may cause cylinders to burst.
2. Incompatibilities: Contact with most metals corrodes them severely and forms flammable hydrogen gas. Contact of hydrogen chloride gas or liquid with any alkali or active metal may develop enough heat to cause fire in adjacent combustible material.
3. Hazardous decomposition products: None
4. Special precautions: Hydrogen chloride will attack most metals and some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Patty notes that according to Hirt, a concentration of 35 ppm "cannot be detected by taste or odor. (Editor's note: Most people can detect 1 to 5 ppm; 5 to 10 ppm is disagreeable)." The editor does not specify how most people can detect 1 to 5 ppm, however.
2. Eye Irritation Level: Grant states that an exposure of animals to "100 ppm for 6 hours daily for 50 days caused only slight unrest and irritation of the eyes, but no injury."
3. Other Information: The *Documentation of TLV's* states that hydrogen chloride is a strong irritant. Thirty-five ppm "caused irritation of the throat on short exposure . . . . Elkins states, however, that hydrogen chloride was immediately irritating when inhaled at concentrations of 5 ppm or more."
4. Evaluation of Warning Properties: Through its irritant effects, hydrogen chloride can be detected at or slightly above the permissible exposure limit. For the purposes of this guideline, therefore, hydrogen chloride 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 hydrogen chloride. 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 hydrogen chloride in a bubbler containing sodium acetate solution, followed by dilution with water, and analysis with an ion-specific electrode. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen chloride may be used. An analytical method for hydrogen chloride 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 mists or solutions of hydrogen chloride which have a pH less than 3.0.

• 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 mists or solutions of hydrogen chloride which have a pH equal to or greater than 3.0.

• Where there is any possibility of exposure of an employee's body to solutions of hydrogen chloride which have a pH less than 3.0, 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 solutions of hydrogen chloride which have a pH less than 3.0 should be removed immediately and not reworn until the hydrogen chloride is removed from the clothing.

• Non-impervious clothing which becomes wet with solutions of hydrogen chloride with a pH equal to or greater than 3.0 should be removed promptly and not reworn until the hydrogen chloride is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of mists of solutions of hydrogen chloride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to solutions of hydrogen chloride which have a pH less than 3.0, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with solutions of hydrogen chloride which have a pH less than 3.0 should be immediately washed or showered to remove any hydrogen chloride.

• Skin that becomes wet with solutions of hydrogen chloride which have a pH equal to or greater than 3.0 should be promptly washed or showered to remove any hydrogen chloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use during pickling of metals including stainless steel, iron, nickel, and monel	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use as a catalyst or chlorinating agent in chemical synthesis; use during metal treatment and fabricating operations in electroplating, acid dipping, stripping, electropolishing, etching, welding, and flame-cutting of metal primed with paint or cleaned with chlorinated hydrocarbons, and used as a gaseous flux in babbitting	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in oxyhydrochlorination processing in production of chlorinated hydrocarbons	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in food processing and manufacture including sugar cane refining, glucose, and corn sugar, and brewing operations	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in industrial chemical cleaning operations; use in production of plastics and resins	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in rubber manufacture including synthesis of chloroprene; use as a chlorinating agent and in coagulation of latex	Local exhaust ventilation; general mechanical ventilation; personal protective equipment

Operation	Controls
Liberation during synthesis of other organic chemicals; use in extraction and reduction processing of metal ores	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use as a deliner of hides in leather manufacture	Local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in activation of petroleum wells; use in waste treatment operations for neutralization of alkaline waste streams; use in production of chlorine	Local exhaust ventilation; general mechanical 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 solutions of hydrogen chloride or strong concentrations of hydrogen chloride 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 solutions of hydrogen chloride or strong concentrations of hydrogen chloride gas get on the skin, immediately flush the contaminated skin with water. If solutions of hydrogen chloride or strong concentrations of hydrogen chloride gas penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of hydrogen chloride, 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 solutions of hydrogen chloride have been swallowed and the person is conscious, give him large amounts of water to dilute the hydrogen chloride. 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 leaks until cleanup has been completed.

• If hydrogen chloride gas 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.

• If solutions of hydrogen chloride are spilled, the following steps should be taken:

1. Collect or confine spilled material in the most convenient and safe manner.
2. If possible, reclaim the spilled material. If this is not possible;
3. dilute and/or neutralize and dispose in a secured sanitary landfill.

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phia, 1958.

RESPIRATORY PROTECTION FOR HYDROGEN CHLORIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration	
50 ppm or less	Any chemical cartridge respirator with an acid gas cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	Any chemical cartridge respirator with a full facepiece and an acid gas cartridge(s). A gas mask with a chin-style or a front- or back-mounted acid gas canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 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 acid gases. 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 hydrogen chloride; 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 100 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Hydrogen Cyanide

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: HCN
- Synonyms: Hydrocyanic acid; prussic acid; formonitrile
- Appearance and odor: Colorless or pale blue liquid or gas with a bitter almond odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen cyanide is 10 parts of hydrogen cyanide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 11 milligrams of hydrogen cyanide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 5 mg cyanide/m^3 averaged over a 10-minute period. The NIOSH Criteria Document for Hydrogen Cyanide and Cyanide Salts should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen cyanide 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**

1. Short-term Exposure: Inhalation, ingestion, or skin absorption of hydrogen cyanide may be rapidly fatal. Larger doses may cause the person to rapidly lose consciousness, stop breathing, and die. At lower levels of exposure, a person may experience weakness, headache, confusion, nausea, and vomiting. These symptoms may be followed by unconsciousness and death. Hydrogen cyanide liquid may irritate the eyes.

2. Long-term Exposure: Effects from chronic exposure to hydrogen cyanide are non-specific and rare.

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 hydrogen cyanide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen cyanide 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 fainting spells, such as occur in various types of cardiovascular and nervous disorders, and and those who are unusually susceptible to effects of anoxia or with anemia would be expected to be at increased risk from exposure. Examination of the cardiovascular, nervous, and upper respiratory systems, and thyroid should be stressed.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

3. First Aid Kits: First aid kits should be immediately available in workplaces where there is a potential for the release of hydrogen cyanide. These kits should contain a minimum of 48 ampules, each of 0.3 ml amyl nitrate, and complete instructions for use. In addition, 2 physician's kits should be immediately available to trained medical personnel. These kits should contain the above quantity of amyl nitrate as well as sterile sodium

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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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nitrite solution (3%) and sterile sodium thiosulfate solution (25%). All of the above drugs should be replaced at least biannually to ensure their potency.

• **Summary of toxicology**

Hydrogen cyanide (HCN) vapor, a source of cyanide ion, is an asphyxiant due to an inhibitory action on metabolic enzyme systems and can be rapidly fatal. Cyanide exerts this effect because it inactivates certain enzymes by forming very stable complexes with the metal in them. Cytochrome oxidase is probably the most important of these since it occupies a fundamental position in the respiratory process and is involved in the ultimate electron transfer to molecular oxygen. Since cytochrome oxidase is present in practically all cells that function under aerobic conditions, and since the cyanide ion diffuses easily to all parts of the body, it is capable of suddenly bringing to a halt practically all cellular respiration. A few inhalations of high concentrations of HCN may be followed by almost instantaneous collapse and cessation of respiration; 270 ppm HCN is immediately fatal to humans, 181 ppm is fatal after 10 minutes, 135 ppm after 30 minutes, and 110 ppm may be fatal in 1 hour. At lower levels of exposure to HCN, the earliest symptoms of intoxication may include weakness, headache, confusion, and occasionally nausea and vomiting; respiratory rate and depth usually increase initially and at later stages become slow and gasping; if cyanosis is present, it usually indicates that respiration has either ceased or has been very inadequate for a few minutes. Humans tolerate 45 to 54 ppm for ½ to 1 hour without immediate or delayed effects, while 18 to 36 ppm may result in some symptoms after an exposure of several hours. The ingestion by humans of 50 to 100 mg of HCN may also be fatal. Eye contact with liquid HCN may cause irritation. Cyanide is one of the few toxic substances for which an antidote exists, and it functions as follows. First, amyl nitrite (inhalation) and sodium nitrite (intravenously) are administered to form methemoglobin, which binds firmly with free cyanide ions. This traps any circulating cyanide ions. The formation of 10 to 20% methemoglobin usually does not involve appreciable risk, yet provides a large amount of cyanide-binding substance. Second, sodium thiosulfate is administered intravenously to increase the rate of conversion of cyanide to the less toxic thiocyanate. Methylene blue should not be administered, because it is a poor methemoglobin former and, moreover, promotes the conversion of methemoglobin back to hemoglobin.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 27
2. Boiling point (760 mm Hg): 26 C (79 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of hydrogen cyanide): 0.93
5. Melting point: −14.4 to −16.8 C (7 to 2 F)
6. Vapor pressure at 20 C (68 F): 620 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: Older samples may polymerize and explode unless acid stabilizer is maintained at proper concentration. Samples containing more than 2 − 5% of water are less stable than dry material. Samples stored more than 90 days are hazardous.
2. Incompatibilities: Contact with bases such as caustics and amines may cause violent polymerization and explosion.
3. Hazardous decomposition products: None more toxic than hydrogen cyanide.
4. Special precautions: Liquid hydrogen cyanide will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: −17.8 C (0 F) (closed cup)
2. Autoignition temperature: 538 C (1000 F)
3. Flammable limits in air, % by volume: Lower: 5.6; Upper: 40
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

• **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor of HCN is usually described as 'sweet'; trained persons describe the odor as that of bitter almonds and can detect it at about one ppm." The Manufacturing Chemists Association (MCA) states that "although hydrocyanic acid has a characteristic odor, its toxic action at hazardous concentrations is so rapid that it is of no value as a warning."
2. Eye Irritation Level: Grant states that "only occasionally has reference been made to an irritation of the eye, conjunctivitis, or superficial keratitis developing after chronic exposure to hydrogen cyanide gas."
3. Evaluation of Warning Properties: For the purposes of this guideline, hydrogen cyanide has been treated as a material with poor warning properties. Although the odor threshold appears to be below the permissible exposure limit, Patty states that "the sense of smell is . . . easily fatigued; and there is wide individual variation in the minimum odor threshold."

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 hydrogen cyanide. 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**

Hydrogen cyanide may be monitored by collection in midget impingers containing sodium hydroxide, followed by analysis with an ion specific electrode. An analytical method for hydrogen cyanide 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 liquid hydrogen cyanide.

• Where there is any possibility of exposure of an employee's body to liquid hydrogen cyanide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Any clothing which becomes wet with, or non-impervious clothing which becomes contaminated with, liquid hydrogen cyanide should be removed immediately and not reworn until the hydrogen cyanide is removed from the clothing.

• Clothing wet with hydrogen cyanide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen cyanide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen cyanide, the person performing the operation should be informed of hydrogen cyanide's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid hydrogen cyanide contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to hydrogen cyanide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with hydrogen cyanide should be immediately washed or showered to remove any hydrogen cyanide.

• Employees who handle hydrogen cyanide 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 hydrogen cyanide may occur and control methods which may be effective in each case:

Operation	Controls
Use in fumigation of structures and agricultural crops	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use of cyanide salts or solutions in metal treatment operations, blast furnace and coke oven operations, metal ore processing, and photoengraving operations	Process enclosure; local exhaust ventilation; personal protective equipment
Use in production of intermediates in synthesis of acrylic plastics, nylon 66, chelating agents, dyes, pharmaceuticals, and specialty chemicals	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 hydrogen cyanide 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 liquid hydrogen cyanide gets on the skin, immediately flush the contaminated skin with water. If liquid hydrogen cyanide soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of hydrogen cyanide, 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 hydrogen cyanide 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 hydrogen cyanide 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 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 reclaimed or collected and atomized in a suitable combustion chamber. Hydrogen cyanide 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 hydrogen cyanide vapors are permitted.

• Waste disposal method:

Liquid hydrogen cyanide may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR HYDROGEN CYANIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 50 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 hydrogen cyanide. 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 hydrogen cyanide; 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 50 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Hydrogen Fluoride

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: HF
- Synonyms: Anhydrous hydrofluoric acid; HF-A
- Appearance and odor: Colorless, fuming liquid or gas with a strong irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen fluoride is 3 parts of hydrogen fluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2 milligrams of hydrogen fluoride per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 2.5 mg fluoride/m^3 averaged over a work shift of not more than 10 hours per day, 40 hours per week, with a ceiling level of 5 mg fluoride/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Hydrogen Fluoride should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen fluoride 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**

1. Short-term Exposure: Hydrogen fluoride liquid or vapor causes severe irritation and deep-seated burns of the eye and eye lids if it comes in contact with the eyes. If the chemical is not removed immediately, permanent visual defects or blindness may result. When lower concentrations (20% or less) come into contact with the skin, the resulting burns do not usually become apparent for several hours. Skin contact with higher concentrations is usually apparent in a much shorter period, if not immediately. The skin burns may be very severe and painful. Hydrofluoric acid is a severe irritant to the nose, throat, and lungs. Severe exposure causes rapid inflammation and congestion of the lungs. Breathing difficulties may not occur until some hours after exposure has ceased. Death may occur from breathing this chemical. If swallowed, hydrofluoric acid will immediately cause severe damage to the throat and stomach.

2. Long-term Exposure: Prolonged or repeated exposure to lower concentrations of hydrogen fluoride vapor may cause changes in the bones. Exposure to low concentrations of vapors of hydrogen fluoride may also cause chronic irritation and congestion of the nose, throat, and bronchial tubes.

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 hydrogen fluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen fluoride 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 eyes, respiratory tract, central nervous system, skeletal system, and the kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in acute overexposures to hydrogen fluoride, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centri-

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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fuged sediment. An analysis for fluoride should be performed.

—Pelvic roentgenogram: Hydrogen fluoride may cause skeletal abnormalities. A radiologic examination of the male pelvis with proper gonadal shielding should be conducted at the time of the preplacement examination and when indicated by analysis of the results of the urinary hydrogen fluoride tests.

—Eye disease: Hydrogen fluoride is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—14" x 17" chest roentgenogram: Hydrogen fluoride may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Hydrogen fluoride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Skin disease: Hydrogen fluoride can cause dermatitis on prolong exposure to concentrations from 1.8 to 8.1 mg/m³. 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, except that the radiologic examination of the pelvis should be conducted only when clinically indicated.

- **Summary of toxicology**

Hydrogen fluoride as a gas is a severe respiratory irritant, and in solution causes severe and painful burns of the skin. Animals repeatedly exposed to 17 ppm showed damage to the lungs, liver, and kidneys, but at 8.6 ppm there was only occasional lung injury. Fatalities occurred in 3 of 6 workers exposed to spills of 70% solutions on the skin and inhalation of the vapor; despite prompt showering with water for skin burns, death from pulmonary edema occurred 2 hours after exposure. A chemist, splashed on the face and upper extremities with hydrogen fluoride, developed pulmonary edema 3 hours after exposure and died 10 hours later. In human subjects, 120 ppm was the highest concentration that could be tolerated for 1 minute, because of the onset of conjunctival and respiratory irritation with stinging of the skin. Repeated experimental human exposures to concentrations of 2 ppm for 6 hours daily caused a slight stinging of the eyes and skin of the face, with nasal irritation. Repeated exposures to low concentrations at work may produce chronic irritation of the nose, throat, and bronchi. Hydrogen fluoride solutions in contact with skin, if untreated, result in marked tissue destruction; the fluoride ion readily penetrates skin and deep tissue, causing necrosis of soft tissues and decalcification of bone. When skin contact is with solutions of less than 50% hydrogen fluoride, the burns do not become manifest immediately; burns from solutions stronger than 50% and anhydrous HF are felt in a matter of minutes, and because fluoride ions penetrate the skin readily, necrosis of deep tissue and damage to the bone may occur. Severe eye injuries from splashes may occur. In one case of eye burns from a fine spray of hydrofluoric acid in the face, considerable loss of corneal epithelium occurred despite immediate and copious flushing with water and irrigation for 3 hours with a 0.5% solution of benzethonium chloride; within 19 days there was recovery of normal vision.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 20
2. Boiling point (760 mm Hg): 19.5 C (67.1 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of hydrogen fluoride): 0.7
5. Melting point: −83.4 C (−118 F)
6. Vapor pressure at 20 C (68 F): 760 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 of hydrogen fluoride (liquid or gas) with metals, concrete, glass, and ceramics causes severe corrosion. Contact with metals may form flammable hydrogen gas.
3. Hazardous decomposition products: None
4. Special precautions: Liquid or gaseous hydrogen fluoride will attack some forms of plastics, rubber, and coatings. It will also attack glass and other ceramic materials.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The Manufacturing Chemists Association reports that the vapor has a sharp and penetrating odor, but no quantitative information is available concerning the odor threshold.
2. Eye Irritation Level: Grant states that "air containing as little as 5 ppm (hydrogen fluoride) causes irritation of the eyes."
3. Other Information: According to Grant, irritation of the nose occurs at a concentration as low as 5 ppm.
4. Evaluation of Warning Properties: Since hydrogen fluoride can be detected through its irritant effects at a concentration slightly above the permissible exposure limit, it is treated as a material with adequate 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 hydrogen fluoride. 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 hydrogen fluoride in a bubbler, followed by dilution with a buffer, and analysis with an ion-specific electrode. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen fluoride may be used. An analytical method for hydrogen fluoride 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 hydrogen fluoride or solutions containing hydrogen fluoride.

• Clothing contaminated with hydrogen fluoride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen fluoride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen fluoride, the person performing the operation should be informed of hydrogen fluoride's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid hydrogen fluoride or solutions containing hydrogen fluoride, 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 hydrogen fluoride should be removed immediately and not reworn until the hydrogen fluoride 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 hydrogen fluoride or solutions containing hydrogen fluoride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid hydrogen fluoride or solutions containing hydrogen fluoride, an eye-wash fountain should be provided within the immediate work area for emergency use.

• Whenever hydrogen fluoride is accidentally released into the workplace air, employees should be required to immediately evacuate the area.

SANITATION

• Skin that becomes contaminated with hydrogen fluoride should be immediately washed or showered to remove any hydrogen fluoride.

• Eating and smoking should not be permitted in areas where liquid hydrogen fluoride or solutions containing hydrogen fluoride are handled, processed, or stored.

• Employees who handle liquid hydrogen fluoride or solutions containing hydrogen fluoride 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 hydrogen fluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of chlorofluorohydrocarbons for application as refrigerant fluids, aerosol propellants, specialty solvents, high-performance plastics, and foaming agents	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in cleaning sandstone and marble; use as a pickling agent for stainless steel and other metals; use as a cleaner in meat packing industry	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in manufacture of aluminum fluoride and synthetic cryolite for reduction of aluminum oxide to aluminum	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in electroplating operations	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from fertilizer manufacture	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid as a catalyst in alkylation of petroleum fractions to produce high-octane fuels	Process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in etching, frosting, and polishing glassware and ceramics	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an acidizing agent during injection of acid into oil wells	Process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in removal of sand and scale from foundry castings	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in separation and purification of uranium isotopes	Process enclsoure; local exhaust ventilation; personal protective equipment
Use in manufacture of insecticides; use of aqueous acid in treating textiles to remove trace metals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in production of fluorosilicone products	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in preparation of microelectronic circuits and quartz crystals for radio oscillators	Process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in manufacture of laundry sours and stain removers	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in extraction and purification of minerals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in manufacture of pharmaceuticals and special dyes	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 hydrogen fluoride or solutions containing hydrogen fluoride 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 hydrogen fluoride or solutions containing hydrogen fluoride get on the skin, immediately flush the contaminated skin with water for a considerable time. If liquid hydrogen fluoride or solutions containing hydrogen fluoride penetrate through the clothing, remove the clothing immediately and flush the skin with water for a considerable time. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of hydrogen fluoride, 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 hydrogen fluoride or solutions containing hydrogen fluoride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the hydrogen fluoride. 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 hydrogen fluoride is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
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, allow to vaporize and disperse the gas.

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RESPIRATORY PROTECTION FOR HYDROGEN FLUORIDE

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Gas or Vapor Concentration	
20 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against hydrogen fluoride. A gas mask with a chin-style or a front- or back-mounted canister and filter providing protection against hydrogen fluoride. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
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	Any gas mask providing protection against hydrogen fluoride. 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 hydrogen fluoride; 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 Hydrogen Peroxide

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: H_2O_2
- Synonyms: High-strength hydrogen peroxide; peroxide; hydrogen dioxide
- Appearance and odor: Colorless liquid with a slightly sharp odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen peroxide is 1 part of hydrogen peroxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1.4 milligrams of hydrogen peroxide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen peroxide 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 vapor from hydrogen peroxide may cause extreme irritation of the eyes, nose, and throat. Splashes of hydrogen peroxide in the eyes may cause severe damage and possible blindness. Eye damage may appear a week or more after exposure. If the liquid is splashed on the skin, it may cause tingling and temporary whitening. If the skin is washed promptly, the skin will return to normal in 2 or 3 hours. If the hydrogen peroxide is not removed, redness and blister formation may result. If swallowed, hydrogen peroxide may cause injury to the mouth and throat with possible bleeding from the esophagus and stomach. The swallowed hydrogen peroxide may produce large quantities of oxygen gas which may distend the esophagus and stomach and cause severe 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 hydrogen peroxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen peroxide 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 hydrogen peroxide exposure.

—Eye disease: Hydrogen peroxide, 90 percent, is an eye irritant. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: Hydrogen peroxide, 90 percent, causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of hydrogen peroxide, 90 percent, might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Hydrogen peroxide, 90 percent, 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**

Ninety percent hydrogen peroxide vapor, mist, or liquid irritates the eyes, mucous membranes, and skin. Repeated exposure of dogs to 7 ppm for 6 months caused sneezing, lacrimation, and bleaching of hair; at autopsy there was local atelectasis. In humans, inhalation of high concentrations of vapor or mist may cause extreme irritation and inflammation of the nose and

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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throat. Exposure for a short period to mist or diffused spray may cause stinging of the eyes and lacrimation. Splashes of the liquid in the eyes may cause severe damage, including ulceration of the cornea; there may be a delayed appearance of damage to the eyes, and corneal ulceration has, on rare occasions, appeared even a week or more after exposure. Skin contact with the liquid for a short time will cause a temporary whitening or bleaching of the skin; if splashes on the skin are not removed, erythema and formation of vesicles may occur. Ingestion may cause irritation of the upper gastrointestinal tract; decomposition of the hydrogen peroxide will result in the rapid liberation of oxygen, which may distend and damage the esophagus or stomach.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 34
2. Boiling point (760 mm Hg): 141 C (286 F) (calculated)
3. Specific gravity (water = 1): 1.38
4. Vapor density (air = 1 at boiling point of hydrogen peroxide): Not applicable (decomposes)
5. Melting point: −11 C (12 F)
6. Vapor pressure at 30 C (86 F): 5 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: Hydrogen peroxide decomposes slowly at ordinary temperatures and builds up pressure if the container is closed. The rate of decomposition doubles for each 10 C rise (1.5 times 10 C rise) in temperature and becomes self-sustaining at 141 C (285 F). Contaminated hydrogen peroxide can decompose at a rate that will exceed the capacity of the vent in the container. Hydrogen peroxide in concentrations up to about 90% does not readily detonate. Higher concentrations or elevated temperatures may facilitate detonation.
2. Incompatibilities: Contact with most organic or readily oxidizable materials and combustibles causes fires and explosions. Contact with iron, copper, brass, bronze, chromium, zinc, lead, manganese, silver, and other catalytic metals (or their salts) causes rapid decomposition with evolution of oxygen gas and heat which may increase container pressure.
3. Hazardous decomposition products: None
4. Special precautions: Liquid hydrogen peroxide will attack some forms of plastics, rubber, and coatings; many will ignite. The adiabatic decomposition temperature is 740 C (1364 F), so that most combustible materials in contact with the decomposition products will readily burst into flames.

• **Flammability**

1. Not combustible, but a powerful oxidizing agent

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of hydrogen peroxide.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "the eyes do not appear to be damaged from exposure to the vapor." Grant reports, "Injuries of human eyes have been rare. Workers exposed to vapors from 90% hydrogen peroxide have noted primarily respiratory irritation, but a splash of such high concentration is generally feared as a potential cause of severe corneal damage . . . .

'Experimental exposure of dogs to 7 ppm hydrogen peroxide in air 6 hours a day caused no adverse effect during 23 weeks but then began to cause sneezing and lacrimation. Rabbits similarly exposed for 10 weeks suffered no corneal damage."

Deichmann and Gerarde, however, note that "vapors are irritating to the eyes, nose and throat."

According to the *Hygienic Guide*, hydrogen peroxide can be "recognized only by irritant effects, especially in nasal passages." They give an irritation threshold of approximately 100 ppm.

3. Evaluation of Warning Properties: Hydrogen peroxide has 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 hydrogen peroxide 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 Enforce-

ment 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 hydrogen peroxide.

• Clothing contaminated with hydrogen peroxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen peroxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen peroxide, the person performing the operation should be informed of hydrogen peroxide's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid hydrogen peroxide, 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 hydrogen peroxide should be removed immediately and not reworn until the hydrogen peroxide 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 hydrogen peroxide contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid hydrogen peroxide, an eyewash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with hydrogen peroxide should be promptly washed or showered to remove any hydrogen peroxide.

• Employees who handle liquid hydrogen peroxide 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 hydrogen peroxide may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of propellants for military and space programs; use as a component of explosives	Process enclosure; general dilution ventilation; personal protective equipment; vented containers; ample available water supply
Use in chemical synthesis as an oxidant in organic and inorganic synthesis	Process enclosure; general dilution ventilation; personal protective equipment vented containers; ample available water supply
Use as a polymerization promoter; use as a bleaching agent for oils, waxes, fats, and discolored concentrated acids	Process enclosure; general dilution ventilation; personal protective equipment vented containers; ample available water supply

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 hydrogen peroxide 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 liquid hydrogen peroxide gets on the skin, immediately flush the contaminated skin with water. If liquid hydrogen peroxide soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention promptly.

• **Breathing**

If a person breathes in large amounts of hydrogen peroxide, 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 hydrogen peroxide 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 hydrogen peroxide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Dilute with copious quantities of water.

• Waste disposal method:

After dilution with copious quantities of water, hydrogen peroxide may be flushed into a sewer.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Hydrogen Peroxide (90%)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR HYDROGEN PEROXIDE (90%)

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.
75 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 75 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-oxidizable sorbents and providing protection against hydrogen peroxide. 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 hydrogen peroxide; 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 75 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Hydrogen Selenide

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: H_2Se
- Synonyms: Selenium hydride
- Appearance and odor: Colorless gas with a very offensive odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen selenide is 0.05 part of hydrogen selenide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of hydrogen selenide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen selenide can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Exposure to hydrogen selenide may cause irritation of the eyes, nose, throat, and lungs, nausea, vomiting, and diarrhea. Subsequently, there may be a metallic taste in the mouth, garlic odor of the breath, dizziness, and extreme tiredness. Hydrogen selenide has been known to cause pneumonia and liver damage 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 hydrogen selenide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen selenide 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 hydrogen selenide exposure.

—Chronic respiratory disease: Hydrogen selenide causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of hydrogen selenide might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Hydrogen selenide 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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Hydrogen selenide gas irritates the eyes, nose, and throat and causes pulmonary irritation in animals. Guinea pigs exposed to 10 ppm for 2 hours exhibited immediate irritation of the eyes and nose; a high percentage of the animals died, apparently from pneumonitis. Exposure of guinea pigs to 1 mg/m^3 (0.3 ppm) for 8 hours produced death in half of the animals; pulmonary irritation and liver damage were observed. In humans, a concentration of 1.5 ppm is said to produce intolerable irritation of the eyes and nose. Five workers exposed to concentrations of less than 0.2 ppm of hydrogen selenide and possibly other selenium compounds for 1 month developed nausea, vomiting, diarrhea, metallic taste in the mouth, garlic odor of the breath, dizziness, lassitude, and fatigability; following cessation of exposure, there was a gradual regression of symptoms during the succeeding months. Urinary selenium levels of the workers

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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ranged from 0 to 13.1 mg Se/100 cc urine; there was no correlation between symptoms and levels of urinary excretion.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 81
2. Boiling point (760 mm Hg): −41.3 C (−42 F)
3. Specific gravity (water = 1): Liquid = 2.1 at boiling point
4. Vapor density (air = 1 at boiling point of hydrogen selenide): 2.8
5. Melting point: −65.7 C (−86.5 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): 0.73
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with oxidizers, acids, water, and halogenated hydrocarbons may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as selenium dioxide fume) may be released in a fire involving hydrogen selenide.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Shut off flow of gas; carbon dioxide

- **Warning properties**

1. Odor Threshold: May and Summer report odor thresholds for hydrogen selenide of 0.3 ppm and 3 ppm, respectively.
2. Irritation Level: Grant states that "a concentration of 1.5 ppm in air is said to produce intolerable irritation of the eyes and nose which tends to limit exposure and safeguard against injury. However, below 1 ppm the ocular and respiratory warning properties are insufficient to prevent exposure which may cause systemic intoxication." Dudley and Miller state that at 0.001 mg/l (0.3 ppm) "no eye or nasal irritation is produced in man."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds of hydrogen selenide are not within three times the permissible exposure limit, hydrogen selenide is treated as a material with poor warning properties. In addition, the AIHA *Hygienic Guide* states that "the odor perception of it (hydrogen selenide) is soon lost."

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 hydrogen selenide 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 hydrogen selenide may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of semi-conductor materials; use in chemical synthesis for metal selenides and organoselenium, lasers, and emulsions	Process enclosure; local exhaust ventilation; personal protective equipment

Liberation from roasting of metal ores and pyrites, production of glass and ceramics, vulcanization of rubber, and etching with inks	Local exhaust ventilation; personal protective equipment
Liberation from overloaded selenium rectifiers	Local exhaust ventilation; personal protective equipment
Liberation from bacterial action of selenium-contaminated clothing	Good personal hygiene practice

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 hydrogen selenide, 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 AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If hydrogen selenide is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak to disperse gas.
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.

• Waste disposal method:

Hydrogen selenide may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Hydrogen Selenide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR HYDROGEN SELENIDE

Condition	Minimum Respiratory Protection* Required Above 0.05 ppm
Gas Concentration	
0.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2 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 2 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 hydrogen selenide. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Hydrogen Sulfide

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: H_2S
- Synonyms: Sulfuretted hydrogen; hydrosulfuric acid; hepatic gas
- Appearance and odor: Colorless gas with a strong odor of rotten eggs. The odor of this gas should not be used as a warning, since its presence may deaden the sense of smell. Hydrogen sulfide can also exist as a liquid at low temperature and high pressure.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen sulfide is a ceiling level of 20 parts of hydrogen sulfide per million parts of air (ppm) or a maximum allowable peak of 50 ppm for 10 minutes once, if no other measurable exposure occurs. NIOSH has recommended that the permissible exposure limit be reduced to 15 mg/m³ (10 ppm) averaged over a 10-minute period, and that work areas in which the concentration of hydrogen sulfide exceeds 70 mg/m³ be evacuated. The NIOSH Criteria Document for Hydrogen Sulfide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen sulfide can affect the body if it is inhaled or if it comes in contact with the eyes, skin, nose or throat. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of high concentrations of hydrogen sulfide vapor may cause loss of consciousness and death. Inhalation of lower concentrations may cause headache, dizziness, and upset stomach. Exposure to hydrogen sulfide can cause temporary loss of the sense of smell, and irritation of the eyes, nose, or throat.

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 hydrogen sulfide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen sulfide 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 eyes and lungs should be stressed.

—Eye disease: Hydrogen sulfide is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—14" x 17" chest roentgenogram: Hydrogen sulfide may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Hydrogen sulfide 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 considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

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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• **Summary of toxicology**

Hydrogen sulfide gas is a rapidly acting systemic poison which causes respiratory paralysis with consequent asphyxia at high concentrations. It irritates the eyes and respiratory tract at low concentrations. Inhalation of high concentrations of hydrogen sulfide, 1000 to 2000 ppm, may cause coma after a single breath and may be rapidly fatal; convulsions may also occur. Exposure to concentrations of hydrogen sulfide above 50 ppm for one hour may produce acute conjunctivitis with pain, lacrimation, and photophobia; in severe form this may progress to keratoconjunctivitis and vesiculation of the corneal epithelium. In low concentrations, hydrogen sulfide may cause headache, fatigue, irritability, insomnia, and gastrointestinal disturbances; in somewhat higher concentrations it affects the central nervous system, causing excitement and dizziness. Prolonged exposure to 250 ppm of hydrogen sulfide may cause pulmonary edema. Prolonged exposure to concentrations of hydrogen sulfide as low as 50 ppm may cause rhinitis, pharyngitis, bronchitis, and pneumonitis. Repeated exposure to hydrogen sulfide results in increased susceptibility, so that eye irritation, cough, and systemic effects may result from concentrations previously tolerated without any effect. Rapid olfactory fatigue can occur at high concentrations.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 34.08
2. Boiling point (760 mm Hg): −60 C (−76 F)
3. Specific gravity (water = 1): Liquid = 1.54
4. Vapor density (air = 1 at 15 C (59 F)): 1.189
5. Melting point: −82.4 C (−116 F)
6. Vapor pressure at 25 C (77 F): 20 atm
7. Solubility in water, g/100 g water at 20 C (68 F): 2.9 (slight)
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers and oxidizing materials may cause fires and explosions. Hydrogen sulfide attacks many metals, which results in the formation of sulfides.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur oxides) may be released in a fire involving hydrogen sulfide.
4. Special precautions: Liquid hydrogen sulfide will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Hydrogen sulfide is a flammable gas.
2. Autoignition temperature: 260 C (500 F)
3. Flammable limits in air, % by volume: Lower: 4.3; Upper: 46
4. Extinguishant: Alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, hydrogen sulfide can be recognized by the "sense of smell at low concentrations. Odor not reliable at high concentrations, and olfactory fatigue occurs quickly . . . . Threshold is 0.13 ppm. Faint but readily perceptible at 0.77 ppm. Easily noticeable at 4.6 ppm. Strong, unpleasant, but not intolerable at 27 ppm." The *Hygienic Guide* also states that "olfactory fatigue can occur with(in) 2 to 15 minutes at 100 ppm."
2. Eye Irritation Level: Grant states that "effects of hydrogen sulfide on the eyes are notable only at sublethal concentrations, most commonly at concentrations so low that they have no discernible systemic effect . . . . Typically, workmen exposed to low concentrations of hydrogen sulfide gas . . . have no sensation of irritation or discomfort for at least several hours, or sometimes for several days while working in the presence of low concentrations. Ocular symptoms generally start after several hours of exposure and may not appear until the patient has finished his work for the day. There is then gradual onset of a scratchy, irritated sensation in the eyes, with tearing and burning . . . . Experimentally it is demonstrable that at a concentration of 100 ppm in air an immediate irritation of the eyes and respiratory tract is produced, but conditions responsible for the vast majority of cases of hydrogen sulfide keratoconjunctivitis are those in which the concentration is too low to cause immediate irritation and has toxic effect only after several hours or days of exposure. However, in industries where the concentration is regularly kept below 10 ppm in air, it is rare to have any irritation of the eyes."

   The *Hygienic Guide* states that "50 to 100 ppm causes slight conjunctivitis and respiratory tract irritation after 1 hour."
3. Evaluation of Warning Properties: Since olfactory fatigue occurs at high concentrations, and since the irritant effects are delayed, hydrogen sulfide is 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 hydrogen sulfide. 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 hydrogen sulfide. Each measurement should consist of a 10-minute sample or a series of consecutive samples totalling 10 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 hydrogen sulfide in an impinger containing an alkaline suspension of cadmium hydroxide, followed by chemical treatment, and spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen sulfide may be used. An analytical method for hydrogen sulfide 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 frozen from contact with liquid hydrogen sulfide or from contact with vessels containing liquid hydrogen sulfide.

• Any clothing which becomes wet with liquid hydrogen sulfide should be removed immediately and not reworn until the hydrogen sulfide has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid hydrogen sulfide may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen sulfide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from pockets during underground mining operations near sulfide ores	Local exhaust ventilation; respiratory protective devices
Liberation during refining of high-sulfur petroleum	Concentration and recovery of H_2SO_4
Liberation from accumulations of decaying organic matter in sewers and waste waters of tanneries, glue factories, fat-rendering plants, and fertilizer plants	Provide continuous water discharge to sewer and cover and vent waste drains
Liberation as a by-product of dehairing and tanning process	Provide separate sewage lines and cover and vent waste drains; add neutralizing agents ($CaCl_2$) as appropriate; local exhaust ventilation
Liberation during manufacture of viscose rayon	Local exhaust ventilation
Liberation during production of sulfur dyes, carbon disulfide, sulfur, oleum, and thioprene	Local exhaust ventilation or process enclosure
Liberation during vulcanization of rubber; during manufacture of coke from coal having high gypsum content	Local exhaust ventilation or process enclosure
Liberation during excavation projects	Respiratory protective equipment

Liberation in closed containers containing organic matter	Respiratory protective equipment; life-support line

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 hydrogen sulfide 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 hydrogen sulfide gets on the skin, immediately flush the contaminated skin with water. If liquid hydrogen sulfide penetrates through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of hydrogen sulfide, 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 LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If hydrogen sulfide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak to disperse gas.
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, allow to vaporize.

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RESPIRATORY PROTECTION FOR HYDROGEN SULFIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
300 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 300 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 acid gases or hydrogen sulfide. Any escape self-contained breathing apparatus.

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

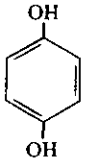
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR HYDROQUINONE

INTRODUCTION

This guideline summarizes pertinent information about hydroquinone 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:** $C_6H_6O_2$
- **Structure:**



- **Synonyms:** 1,4-Benzenediol; dihydroxybenzene; hydroquinol; quinol
- **Identifiers:** CAS 123-31-9; RTECS MX3500000; DOT 2662
- **Appearance and odor:** Colorless to white crystalline solid with no odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 110.11
2. Boiling point (at 760 mmHg): 285°C (545°F)
3. Specific gravity (water = 1): 1.332
4. Vapor density (air = 1 at boiling point of hydroquinone): 3.81
5. Melting point: 173°C (344°F)
6. Vapor pressure at 25°C (77°F): 1.8×10^{-5} mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): 7
8. Evaporation rate (butyl acetate = 1): 1.8×10^{-6}

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving hydroquinone.
3. Caution: Airborne hydroquinone may be oxidized to quinone ($C_6H_4O_2$) at ordinary room temperatures in the presence of moisture.

- **Flammability**

1. Flash point: 165°C (329°F) (closed cup)
2. Autoignition temperature: 516°C (960°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: Based on lack of information on odor threshold and eye irritation levels, hydroquinone should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for hydroquinone is 2 milligrams of hydroquinone 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) is 2 mg/m^3 [0.44 parts of hydroquinone per million parts of air (ppm)] as a ceiling concentration determined in any 15-minute sampling period. In those situations in which workers may be exposed to hydroquinone as a component of other materials at a concentration of 5% or less by weight, it should not be necessary to comply with the provisions of the standard; however; protection of workers' health should be insured by avoiding excessive contact with the chemical and by following effective cleaning procedures. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 2 mg/m^3 as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for hydroquinone

	Exposure limits ppm	Exposure limits mg/m^3
OSHA PEL TWA	—	2
NIOSH REL ceiling (15 min)	0.44	2
ACGIH TLV® TWA	—	2

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

HEALTH HAZARD INFORMATION

• **Routes of exposure**

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

• **Summary of toxicology**

1. *Effects on animals:* Acute subcutaneous injection or oral administration of hydroquinone to multiple species of animals produced hypersensitivity to external stimuli, hyperactive reflexes, breathing difficulty (dyspnea), and bluish discoloration of skin and mucous membranes (due to methemoglobinemia), followed by convulsions, reduced body temperature, paralysis, loss of reflexes, coma, and death (due to decreased oxygen in the blood and respiratory failure). Subchronic or chronic exposure of multiple species of animals by the same routes of administration produced jaundice, anemia, hypoglycemia, increased white blood cell counts, increased cell fragility, depigmentation of skin or fur, and marked weight loss. Subchronic subcutaneous injection of hydroquinone into male rats caused reduction in the weights of sexual organs, sperm production, and fertility (as determined by reduced pregnancies). In mutagenicity tests, hydroquinone damaged DNA and chromosomes in bacteria.

2. *Effects on humans:* Chronic exposure of the eyes to hydroquinone has caused ulceration, opacity, and structural changes.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to hydroquinone can cause headache, dizziness, nausea, vomiting, increased respiration, breathing difficulty, sensation of suffocation, ringing noise in ears, paleness, bluish discoloration of skin, green or brownish-green discoloration of urine, and irritation of the skin and eyes.

2. *Long-term (chronic):* Exposure to hydroquinone can cause depigmentation of the skin, brownish discoloration of the cornea, and blurred vision.

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 hydroquinone, 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, gastrointestinal tract, 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 hydroquinone 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 skin and 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 hydroquinone. 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, gastrointestinal tract, 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.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations

of hydroquinone. 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 hydroquinone with cellulose ester membrane filters followed by treatment with aqueous acetic acid and analysis by high-pressure liquid chromatography. A detailed sampling and analytical method for hydroquinone may be found in the *NIOSH Manual of Analytical Methods* (method number 5004).

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 hydroquinone.

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

SANITATION

Clothing which is contaminated with hydroquinone 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 hydroquinone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of hydroquinone's hazardous properties.

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

Skin that becomes contaminated with hydroquinone 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 hydroquinone 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 hydroquinone 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 hydroquinone

Operations	Controls
During the preparation and use of photographic developers; during use in the dyeing and fur processing industries	Personal protective equipment
During use as an antioxidant; during use as a chemical stabilizer	Local exhaust ventilation, personal protective equipment
During the synthesis of hydroquinone ethers, vitamin E, hydroquinone diacetate, or p-methoxyphenol; during the synthesis and handling of hydroquinone powders	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 hydroquinone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If hydroquinone 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 hydroquinone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If hydroquinone gets on the skin, wash it immediately with soap and water. If hydroquinone 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 hydroquinone is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Hydroquinone solid may be collected and placed in an appropriate container.
4. Hydroquinone solid or liquid 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.
5. For small quantities of liquids containing hydroquinone, 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 hydroquinone vapors. Burn the paper in a suitable location away from combustible materials.
6. Large quantities of liquids containing hydroquinone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Hydroquinone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

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 hydroquinone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 50 mg/m³	Any powered air-purifying respirator with a dust filter (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 100 mg/m³	Any air-purifying full facepiece respirator with a high-efficiency particulate filter
	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 a high-efficiency particulate filter (substance causes eye irritation or damage—eye protection needed)
	Any supplied air respirator with tight-fitting facepiece operated in a continuous flow mode (substance causes eye irritation or damage—eye protection needed)
Less than or equal to 200 mg/m³	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 200 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 0.44 ppm (2 mg/m³) (ceiling).

Occupational Health Guideline for Iodine

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: I_2
- Synonyms: None
- Appearance and odor: Violet solid with a sharp, characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for iodine is a ceiling level of 0.1 part of iodine per million parts of air (ppm). This may also be expressed as 1 milligram of iodine per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Iodine 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: Iodine vapor is a severe irritant of the eyes, respiratory tract, and to a lesser extent, the skin. It may cause severe breathing difficulties which may be delayed in onset. Swallowing iodine may cause burning in the mouth, vomiting, abdominal pain, and diarrhea. Death may result. Crystalline iodine or strong solutions of iodine may cause severe irritation of the skin. It is not easily removed from the skin and may cause burns. An allergic skin rash may occur. It may cause irritation, brown staining, and burning of the eyes.

2. Long-term Exposure: Chronic absorption of iodine may cause insomnia, inflammation of the eyes and nose, bronchitis, tremor, rapid heart beat, diarrhea, and weight loss.

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 iodine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to iodine 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 thyroid disorders, asthma, allergies, or known sensitization to iodine would be expected to be at increased risk from exposure. Examination of the respiratory tract, eyes, nervous system, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Iodine causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Iodine 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**

Iodine vapor is a severe irritant of the eyes, respiratory tract, and, to a lesser extent, the skin. Intratracheal administration to dogs of the vapor from 36 mg iodine/kg body weight was fatal after about 3 hours; the animals developed cough, dyspnea, and rales; autopsy findings were pulmonary edema, subpleural hemorrhage, and an increased iodine content of the thyroid

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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 urine. Workers exposed to an unspecified concentration experienced a burning sensation in the eyes, lacrimation, blepharitis, rhinitis, stomatitis, and chronic pharyngitis; after accidental exposure in a laboratory, technicians reported headache and a feeling of tightness in the chest. Iodine absorbed by the lungs is changed to iodide and eliminated mainly in the urine; iodine is an essential element in nutrition and is required by the thyroid. Accidental ingestion of 2 to 3 g may be fatal; chronic absorption of iodine causes "iodism," a disease characterized by insomnia, conjunctivitis, rhinitis, bronchitis, tremor, tachycardia, parotitis, diarrhea, and weight loss. In an experimental investigation, four human subjects tolerated 0.57 ppm iodine vapor for 5 minutes without eye irritation, but all experienced eye irritation in 2 minutes at 1.63 ppm. In patients exposed to air saturated with iodine vapor for 3 to 4 minutes for therapeutic purposes, there was brown staining of the corneal epithelium and subsequent spontaneous loss of the layer of tissue; recovery occurred within 2 to 3 days. Iodine in crystalline form or in strong solutions is a severe skin irritant; it is not easily removed from the skin, and the lesions resemble thermal burns. Hypersensitivity to iodine characterized by a skin rash has been reported. Iodine is absorbed through the skin in small amounts from a tincture or from vapor applied to the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 253.8
  2. Boiling point (760 mm Hg): 184 C (363 F)
  3. Specific gravity (water = 1): 4.9
  4. Vapor density (air = 1 at boiling point of iodine): 9
  5. Melting point: 113.6 C (237 F)
  6. Vapor pressure at 20 C (68 F): 0.3 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.03
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None hazardous
  2. Incompatibilities: Contact of iodine with gaseous or aqueous ammonia forms a water-insoluble solid that is very sensitive to shock when dry and which will explode, causing fires. Contact with acetylene, acetaldehyde, powdered aluminum, or other active metals may cause fires and explosions.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible by itself, but can react vigorously with reducing materials
- **Warning properties**
  1. Odor Threshold: No quantitative information is available concerning the odor threshold of iodine.
  2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "irritation rather than systemic action limits the concentrations of iodine vapor which can be tolerated. An earlier report states that 0.1 ppm is tolerable, whereas 0.3 ppm is not, but no time limits were furnished in the citation. In a recent investigation, four human subjects tolerated 0.57 ppm iodine vapor for 5 minutes without eye irritation, but all experienced eye irritation in 2 minutes at 1.63 ppm." The eye irritation threshold data reported are not consistent.
  3. Evaluation of Warning Properties: Since the *Hygienic Guide* states that "the warning properties of iodine vapor are not adequate to prevent excessive inhalation exposure," iodine has been treated as a material with poor warning properties. The ILO also notes that the warning properties of iodine vapor cannot be depended upon to prevent excessive exposure. In addition, a recent investigation has shown that a 5-minute exposure to 0.57 ppm iodine vapor did not produce eye irritation in human subjects.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of iodine. 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 iodine 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 solid iodine or liquids containing more than 7% iodine by weight.
- 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 containing 7% or less of iodine by weight.
- If employees' clothing has had any possibility of being contaminated with solid iodine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with iodine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of iodine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the iodine, the person performing the operation should be informed of iodine's hazardous properties.
- Where there is any possibility of exposure of an employee's body to solid iodine or liquids containing more than 7% iodine 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 iodine should be removed immediately and not reworn until the iodine is removed from the clothing.
- Non-impervious clothing which becomes wet with liquids containing 7% or less of iodine by weight should be removed promptly and not reworn until the iodine 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 solid iodine or liquids containing more than 7% iodine by weight contacting the eyes.
- Employees should be provided with and required to use splash-proof safety goggles where liquids containing 7% or less of iodine by weight may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid iodine or liquids containing more than 7% iodine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with solid iodine or liquids containing more than 7% iodine by weight should be immediately washed or showered with soap or mild detergent and water to remove any iodine.
- Skin that becomes wet with solutions containing 7% or less of iodine by weight should be promptly washed or showered with soap or mild detergent and water to remove any iodine.
- Eating and smoking should not be permitted in areas where solid iodine is handled, processed, or stored.
- Employees who handle solid iodine or liquids containing iodine 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 iodine may occur and control methods which may be effective in each case:

Operation	Controls
Use in synthesis of chemical intermediates, pharmaceuticals, photographic chemicals, antiseptics, disinfectants, detergent sanitizers, and organic and inorganic compounds	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a reagent in analytical chemistry; as catalytst in organic synthesis; synthesis of dyes, food additives, and coloring agents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in production of intermediates in purification of metals; use as a catalyst in the modification of selenium during manufacture of photoelectric cells and rectifiers	Process enclosure; local exhaust ventilation; personal protective equipment
Use during manufacture of specialty lubricants and in production of steriospecific polymers	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 iodine, liquids containing iodine, or strong concentrations of iodine 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 iodine or liquids containing iodine get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If iodine or liquids containing iodine penetrate 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 iodine, 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 iodine or liquids containing iodine 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. (If milk is immediately available, give the person milk instead of water).

• **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 iodine 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 iodine should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Iodine may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Iodine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR IODINE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Vapor or Particulate Concentration	
1 ppm or 10 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or 50 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 ppm or 100 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 10 ppm or 100 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 Iron Oxide 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: Fe_2O_3
- Synonyms: Ferric oxide fume
- Appearance: Red-brown fume with a metallic taste

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for iron oxide fume is 10 milligrams of iron oxide 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 iron oxide fume a Threshold Limit Value of 5 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Iron oxide fume can affect the body if it is inhaled.

- **Effects of overexposure**

Repeated exposure to iron oxide fume over a period of years may cause x-ray changes of the lungs, but does not cause the exposed person to become ill.

- **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 iron oxide fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to iron oxide 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 should be stressed.

—14" x 17" chest roentgenogram: Iron oxide fume causes an apparently benign pneumoconiosis. However, since exposure may be associated with other more toxic dust exposures, surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Iron oxide fume causes an apparently benign pneumoconiosis. However, since exposure may be associated with other more toxic dust exposures, 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.

- **Summary of toxicology**

Inhalation of iron oxide fume or dust causes an apparently benign pneumoconiosis termed siderosis. Iron oxide alone does not cause fibrosis in the lungs of animals, and the same probably applies to humans. Exposures of 6 to 10 years are usually considered necessary before changes recognizable by x-ray can occur; the retained dust gives x-ray shadows that may be indistinguishable from fibrotic pneumoconiosis. Eight of 25 welders exposed chiefly to iron oxide for an average of 18.7 (range 3 to 32) years had reticulonodular shadows on chest x-rays consistent with siderosis but no reduction in pulmonary function; exposure levels ranged from 0.65 to 47 mg/m^3. In another study, 16 welders with an average exposure of 17.1 (range 7 to 30) years also had x-rays suggesting siderosis and spirograms which were normal; however, the static and functional compliance of the lungs was reduced; some of the welders were smokers. The welders with the lowest compliance complained of dyspnea.

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: 159.7
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): Solid = 5.24
  4. Vapor density (air = 1 at boiling point of iron oxide fume): Not applicable
  5. Melting point: 1566 C (2850 F) (decomposes)
  6. Vapor pressure at 20 C (68 F): 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 of iron oxide fume with calcium hypochlorite may cause explosions.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Iron oxide fume 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 iron oxide fume on a filter, followed by atomic absorption spectrophotometric analysis. An analytical method for iron oxide 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 iron oxide fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation in production of steel ingots; processing of iron ore to pig iron; heating and pouring of molten metal in foundry operations; hot rolling sheet and strip steel; fettling of castings in foundry operations; during forging of metal items containing iron/steel; pressing of metal items, grinding and polishing of glass, precious metals, stones, and gem stones	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 iron oxide 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 iron oxide fume are inadvertantly released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Iron Oxide Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR IRON OXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 10 mg/m³
Particulate Concentration	
100 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
500 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.
5,000 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 5,000 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 Isoamyl Acetate

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: $CH_3COOCH_2CH_2CH(CH_3)_2$
- Synonyms: Banana oil; 3-methyl-1-butanol acetate; 2-methylbutyl ethanoate
- Appearance and odor: Clear, colorless liquid with a banana-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isoamyl acetate is 100 parts of isoamyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 525 milligrams of isoamyl acetate per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isoamyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to isoamyl acetate may cause irritation of the eyes, nose, and throat. Overexposure may also cause headache, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure 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 isoamyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isoamyl acetate 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 isoamyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isoamyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Isoamyl acetate 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 isoamyl acetate 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 isoamyl acetate 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**

The toxicologic effects of isoamyl acetate are probably similar to those of amyl acetate: chiefly irritation of the conjunctiva and upper respiratory tract, followed by gradual onset of narcosis, with slow recovery after exposure ceases. Men exposed to 950 ppm for 30 minutes reported only irritation of the nose and throat, headache, and weakness; cats exposed to 1900 ppm for 2 to 3 hours per day for a week showed only irritation, weakness, and loss of weight; dogs exposed to 5000 ppm

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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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for 1 hour had nasal irritation and drowsiness. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 130.2
  2. Boiling point (760 mm Hg): 145.6 C (294 F)
  3. Specific gravity (water = 1): 0.87
  4. Vapor density (air = 1 at boiling point of isoamyl acetate): 4.5
  5. Melting point: −100 C (−148 F)
  6. Vapor pressure at 20 C (68 F): 4 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
  8. Evaporation rate (butyl acetate = 1): 0.42
- **Reactivity**
  1. Conditions contributing to instability: Heat
  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 isoamyl acetate.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 25 C (77 F) (closed cup)
  2. Autoignition temperature: 360 C (680 F)
  3. Flammable limits in air, % by volume: Lower: 1.0 (at 100 C (212 F)); Upper: 7.5
  4. Extinguishant: Dry chemical, carbon dioxide, foam
- **Warning properties**
  1. Odor Threshold: By analogy to amyl acetate, which has an odor threshold of 7 ppm (*Handbook of Industrial Organic Solvents*), the odor of isoamyl acetate is assumed to be detectable below the permissible exposure limit (100 ppm).
  2. Eye Irritation Level: The *Handbook of Industrial Organic Solvents* indicates that significant eye and nose irritation does not occur below the threshold limit.
  3. Other Information: According to the *Documentation of TLV's*, the "threshold limit of 100 ppm is recommended to prevent significant irritation of the respiratory passages."
  4. Evaluation of Warning Properties: For the purposes of this guideline, isoamyl acetate 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 isoamyl acetate 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 isoamyl acetate may be used. An analytical method for isoamyl acetate 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 isoamyl acetate.
- Clothing wet with liquid isoamyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isoamyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isoamyl acetate, the person performing the operation should be informed of isoamyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid isoamyl acetate should be removed immediately and not reworn until the isoamyl acetate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid isoamyl acetate may contact the eyes.

SANITATION

• Skin that becomes wet with liquid isoamyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any isoamyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isoamyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray application of varnishes and nitrocellulose lacquers as protective and finish coatings for wood, especially in furniture industry, and on plastic, metal leather, and other surfaces	Local exhaust ventilation; personal protective equipment
Liberation during application of varnishes and nitrocellulose lacquers as protective and finish coatings for wood, paper, metal, leather, and other surfaces by dipping, roller coating, tumbling, knifing, or brushing	General dilution ventilation; local exhaust ventilation
Liberation during air or oven-drying of varnishes and lacquers	General dilution ventilation
Liberation during application of cellulosic adhesives by machine spraying, dipping, roller coating, tumbling, knifing, or brushing in shoe manufacturing, book binding, packaging, leather processing, paper processing, and textile	General dilution ventilation; local exhaust ventilation
Liberation during manual application of cellulosic adhesives, including household cements	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during manufacture of shoe polish and furniture polish; during fermentation of whiskey grains	General dilution ventilation
Liberation during manufacture of cellulosic photographic film by formation from solvent solutions	General dilution ventilation; local exhaust ventilation
Liberation during preparation of perfumes, foods, and other materials for use as flavoring or odorant	General dilution ventilation
Liberation during use as an extractant in purification of pharmaceuticals, including penicillin	General dilution ventilation; local exhaust ventilation
Liberation during cleaning and maintenance of acetate-processing equipment, such as kettles, distillation columns, and storage vessels	Personal protective equipment
Liberation during manufacture of bath sponges	General dilution ventilation
Liberation during manufacture of artificial leathers	General dilution ventilation; local exhaust ventilation
Liberation during manufacture of artificial silk, rayon, and pearls; during manufacture and use of bronzing fluids	General dilution ventilation; local exhaust ventilation
Liberation during use in dry cleaning preparations	General dilution ventilation
Use in treating of natural leathers by tanning	General dilution ventilation; local exhaust ventilation; personal protective equipment

Liberation during drying, dry printing, and other finishing processes for textiles; during application of phosphorus in manufacture of fluorescent lamps	General dilution ventilation; 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 isoamyl acetate 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 isoamyl acetate gets on the skin, promptly flush the contaminated skin with water. If isoamyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of isoamyl acetate, 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 isoamyl acetate 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 isoamyl acetate 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. Isoamyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Isoamyl acetate 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: "Isoamyl Acetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR ISOAMYL ACETATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
3000 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 3000 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 Isoamyl Alcohol

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: $(CH_3)_2CHCH_2CH_2OH$
- Synonyms: 3-Methyl-1-butanol; isobutylcarbinol; isopentyl alcohol; fermentation amyl alcohol; fusel oil
- Appearance and odor: Colorless liquid with an alcoholic odor that causes coughing.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isoamyl alcohol is 100 parts of isoamyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 360 milligrams of isoamyl alcohol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isoamyl alcohol 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 isoamyl alcohol may cause irritation of the eyes and respiratory tract, headache, dizziness, shortness of breath, cough, nausea, vomiting, and diarrhea. Double vision, deafness, delerium, and death may occur. Coma, sugar in the urine, and blood changes have also been reported.
2. Long-term Exposure: Drying and cracking of the skin may result from prolonged or repeated skin exposure.
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 isoamyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isoamyl alcohol 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 isoamyl alcohol exposure.

—Skin disease: Isoamyl alcohol 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 isoamyl alcohol 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 isoamyl alcohol 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 isoamyl alcohol 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**

Isoamyl alcohol vapor is a mild irritant. Among the few reports of experience with the amyl alcohols, exposure of rats to vapor at 8000 ppm was not lethal. Chemically related alcohols are considered to have predominantly narcotic properties at high concentrations. Slight throat irritation has been observed in unacclimated subjects at 100 ppm and objectionable irritation of the eyes, nose, and throat at higher concentrations. No chronic system-

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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ic effects from isoamyl alcohol have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 88
  2. Boiling point (760 mm Hg): 132 C (270 F)
  3. Specific gravity (water = 1): 0.8
  4. Vapor density (air = 1 at boiling point of isoamyl alcohol): 3.0
  5. Melting point: −117 C (−179 F)
  6. Vapor pressure at 20 C (68 F): 2 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 2.4
  8. Evaporation rate (butyl acetate = 1): 0.2
- **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 isoamyl alcohol.
  4. Special precautions: Isoamyl alcohol will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 42.8 C (109 F) (closed cup)
  2. Autoignition temperature: 350 C (662 F)
  3. Flammable limits in air, % by volume (at 212 F): Lower: 1.2; Upper: 9.0
  4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Quantitative information concerning the odor threshold is not available. The *Handbook of Industrial Solvents*, however, states that the odor of n-amyl alcohol is "apparent at approximately 60 ppm." May reports an odor threshold for amyl alcohol of 35 ppm, and Summer reports 10 ppm. By analogy, it is assumed that the odor of isoamyl alcohol is also below the TLV.
  2. Irritation Levels: Patty states that "according to Nelson et al., the following concentrations of 3-methyl-1-butanol (isoamyl alcohol) caused irritation of the respective mucous membranes of the majority of persons subjected to exposure for a few minutes: eyes, 150 ppm (0.54 mg/l); nose, 150 ppm; and throat, 100 ppm (0.36 mg/l)."
  3. Evaluation of Warning Properties: Because of its irritant effects and its odor, isoamyl alcohol 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 isoamyl alcohol 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 isoamyl alcohol may be used. An analytical method for isoamyl alcohol 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 isoamyl alcohol.
- Clothing wet with liquid isoamyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isoamyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isoamyl alcohol, the person performing the operation should be informed of isoamyl alcohol's hazardous properties.
- Non-impervious clothing which becomes wet with liquid isoamyl alcohol should be removed promptly and

not reworn until the isoamyl alcohol is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid isoamyl alcohol may contact the eyes.

SANITATION

• Skin that becomes wet with liquid isoamyl alcohol should be promptly washed or showered with soap or mild detergent and water to remove any isoamyl alcohol.

• Employees who handle liquid isoamyl alcohol 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 isoamyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Use as a vehicle, latent, or diluent solvent during application of paints, lacquers, varnishes, thinners, and paint removers	Local exhaust ventilation; general dilution ventilation
Use in synthesis of drugs and medicinals, as a solvent for alkaloids, and as an extractant of antibiotics in pharmaceutical industry	Local exhaust ventilation; general dilution ventilation
Use in manufacture of lacquers, paints, varnishes, thinners, and paint removers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in organic synthesis of photographic chemicals, isoamyl acetate, and other esters	Local exhaust ventilation; general dilution ventilation; enclosed process; personal protective equipment
Liberation during manufacture and use of printing inks	Local exhaust ventilation; general dilution ventilation
Use as a solvent for resins, gums, waxes, and oils – perfumes, explosives, shoe cement, analytical determination for fat in milk, and artificial rubber	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during manufacture and use in antifoaming agents and carburing fluids	Local exhaust ventilation; general dilution ventilation
Use in mining industry as a frothing agent for flotation of non-ferrous ores	Local exhaust ventilation; general dilution ventilation
Use as a vehicle solvent for celloidin solutions in microscopy	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 isoamyl alcohol 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 isoamyl alcohol gets on the skin, promptly flush the contaminated skin with water. If isoamyl alcohol 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 isoamyl alcohol, 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 isoamyl alcohol 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 isoamyl 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, 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. Isoamyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Isoamyl alcohol 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: "Isoamyl Alcohol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.

• *Handbook of Organic Industrial Solvents*, Technical Guide No. 6 (4th ed.), American Mutual Insurance Alliance, Chicago, 1972.

• May, J.: "Solvent Odor Thresholds for the Evaluation of Solvent Odors in the Atmosphere," *Staub-Reinhalt*, 26:9, 385-389, 1966.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Smyth, H. F., Jr.: "Improved Communication — Hygienic Standards for Daily Inhalation," *Industrial Hygiene Quarterly*, 17:145-146, June 1956.

• Summer, W.: *Odor Pollution of Air: Causes and Control*, L. Hill, London, 1975.

• Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Material Safety Data Sheet – Isoamyl Alcohol*, New York, 1972.

RESPIRATORY PROTECTION FOR ISOAMYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 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.

Occupational Health Guideline for Isoamyl Alcohol

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: $(CH_3)_2CHCH_2CH_2OH$
- Synonyms: 3-Methyl-1-butanol; isobutylcarbinol; isopentyl alcohol; fermentation amyl alcohol; fusel oil
- Appearance and odor: Colorless liquid with an alcoholic odor that causes coughing.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isoamyl alcohol is 100 parts of isoamyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 360 milligrams of isoamyl alcohol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isoamyl alcohol 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 isoamyl alcohol may cause irritation of the eyes and respiratory tract, headache, dizziness, shortness of breath, cough, nausea, vomiting, and diarrhea. Double vision, deafness, delerium, and death may occur. Coma, sugar in the urine, and blood changes have also been reported.
2. Long-term Exposure: Drying and cracking of the skin may result from prolonged or repeated skin exposure.
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 isoamyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isoamyl alcohol 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 isoamyl alcohol exposure.

—Skin disease: Isoamyl alcohol 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 isoamyl alcohol 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 isoamyl alcohol 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 isoamyl alcohol 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**

Isoamyl alcohol vapor is a mild irritant. Among the few reports of experience with the amyl alcohols, exposure of rats to vapor at 8000 ppm was not lethal. Chemically related alcohols are considered to have predominantly narcotic properties at high concentrations. Slight throat irritation has been observed in unacclimated subjects at 100 ppm and objectionable irritation of the eyes, nose, and throat at higher concentrations. No chronic system-

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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ic effects from isoamyl alcohol have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 88
  2. Boiling point (760 mm Hg): 132 C (270 F)
  3. Specific gravity (water = 1): 0.8
  4. Vapor density (air = 1 at boiling point of isoamyl alcohol): 3.0
  5. Melting point: −117 C (−179 F)
  6. Vapor pressure at 20 C (68 F): 2 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 2.4
  8. Evaporation rate (butyl acetate = 1): 0.2
- **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 isoamyl alcohol.
  4. Special precautions: Isoamyl alcohol will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 42.8 C (109 F) (closed cup)
  2. Autoignition temperature: 350 C (662 F)
  3. Flammable limits in air, % by volume (at 212 F): Lower: 1.2; Upper: 9.0
  4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Quantitative information concerning the odor threshold is not available. The *Handbook of Industrial Solvents*, however, states that the odor of n-amyl alcohol is "apparent at approximately 60 ppm." May reports an odor threshold for amyl alcohol of 35 ppm, and Summer reports 10 ppm. By analogy, it is assumed that the odor of isoamyl alcohol is also below the TLV.
  2. Irritation Levels: Patty states that "according to Nelson et al., the following concentrations of 3-methyl-1-butanol (isoamyl alcohol) caused irritation of the respective mucous membranes of the majority of persons subjected to exposure for a few minutes: eyes, 150 ppm (0.54 mg/l); nose, 150 ppm; and throat, 100 ppm (0.36 mg/l)."
  3. Evaluation of Warning Properties: Because of its irritant effects and its odor, isoamyl alcohol 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 isoamyl alcohol 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 isoamyl alcohol may be used. An analytical method for isoamyl alcohol 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 isoamyl alcohol.
- Clothing wet with liquid isoamyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isoamyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isoamyl alcohol, the person performing the operation should be informed of isoamyl alcohol's hazardous properties.
- Non-impervious clothing which becomes wet with liquid isoamyl alcohol should be removed promptly and

not reworn until the isoamyl alcohol is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid isoamyl alcohol may contact the eyes.

SANITATION

• Skin that becomes wet with liquid isoamyl alcohol should be promptly washed or showered with soap or mild detergent and water to remove any isoamyl alcohol.

• Employees who handle liquid isoamyl alcohol 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 isoamyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Use as a vehicle, latent, or diluent solvent during application of paints, lacquers, varnishes, thinners, and paint removers	Local exhaust ventilation; general dilution ventilation
Use in synthesis of drugs and medicinals, as a solvent for alkaloids, and as an extractant of antibiotics in pharmaceutical industry	Local exhaust ventilation; general dilution ventilation
Use in manufacture of lacquers, paints, varnishes, thinners, and paint removers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in organic synthesis of photographic chemicals, isoamyl acetate, and other esters	Local exhaust ventilation; general dilution ventilation; enclosed process; personal protective equipment
Liberation during manufacture and use of printing inks	Local exhaust ventilation; general dilution ventilation
Use as a solvent for resins, gums, waxes, and oils – perfumes, explosives, shoe cement, analytical determination for fat in milk, and artificial rubber	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during manufacture and use in antifoaming agents and carburing fluids	Local exhaust ventilation; general dilution ventilation
Use in mining industry as a frothing agent for flotation of non-ferrous ores	Local exhaust ventilation; general dilution ventilation
Use as a vehicle solvent for celloidin solutions in microscopy	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 isoamyl alcohol 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 isoamyl alcohol gets on the skin, promptly flush the contaminated skin with water. If isoamyl alcohol 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 isoamyl alcohol, 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 isoamyl alcohol 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 isoamyl 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, 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. Isoamyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Isoamyl alcohol 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: "Isoamyl Alcohol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.

• *Handbook of Organic Industrial Solvents*, Technical Guide No. 6 (4th ed.), American Mutual Insurance Alliance, Chicago, 1972.

• May, J.: "Solvent Odor Thresholds for the Evaluation of Solvent Odors in the Atmosphere," *Staub-Reinhalt*, 26:9, 385-389, 1966.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Smyth, H. F., Jr.: "Improved Communication — Hygienic Standards for Daily Inhalation," *Industrial Hygiene Quarterly*, 17:145-146, June 1956.

• Summer, W.: *Odor Pollution of Air: Causes and Control*, L. Hill, London, 1975.

• Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Material Safety Data Sheet – Isoamyl Alcohol*, New York, 1972.

RESPIRATORY PROTECTION FOR ISOAMYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 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.

Occupational Health Guideline for Isobutyl Acetate

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: $CH_3COOCH_2CH(CH_3)_2$
- Synonyms: 2-Methylpropyl acetate; beta-methylpropyl ethanoate; acetic acid isobutyl ester
- Appearance and odor: Clear, colorless liquid with a pleasant, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isobutyl acetate is 150 parts of isobutyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 700 milligrams of isobutyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isobutyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to isobutyl acetate may cause irritation of the eyes, nose, and throat. Severe overexposure may cause weakness, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure may produce 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 isobutyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isobutyl acetate 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 isobutyl acetate exposure.

—Skin disease: Isobutyl acetate is a mild 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 isobutyl acetate 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 isobutyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Although isobutyl acetate 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**

The principal effects of overexposure to isobutyl acetate are irritation of the eyes and nose. Narcosis occurs at high concentrations. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 116
  2. Boiling point (760 mm Hg): 117 C (243 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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3. Specific gravity (water = 1): 0.87
4. Vapor density (air = 1 at boiling point of isobutyl acetate): 4.0
5. Melting point: −97 C (−143 F)
6. Vapor pressure at 20 C (68 F): 13 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.67
8. Evaporation rate (butyl acetate = 1): 1.5

• **Reactivity**

1. Conditions contributing to instability: Heat
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 isobutyl acetate.
4. Special precautions: Isobutyl acetate will dissolve a wide variety of resins and plastics.

• **Flammability**

1. Flash point: 18 C (64 F) (closed cup)
2. Autoignition temperature: 421 C (790 F)
3. Flammable limits in air, % by volume: Lower: 2.4; Upper: 10.5
4. Extinguishant: Dry chemical, carbon dioxide, foam

• **Warning properties**

1. Odor Threshold: Summer and May both report an odor threshold for isobutyl acetate of 4 ppm.
2. Eye Irritation Level: According to the *Documentation of TLV's*, the TLV of 150 ppm "is recommended primarily to prevent irritation of eyes and respiratory passages."
3. Evaluation of Warning Properties: Since the odor threshold of isobutyl acetate is below the permissible exposure limit, 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 isobutyl acetate 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 isobutyl acetate may be used. An analytical method for isobutyl acetate 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 isobutyl acetate.

• Clothing wet with liquid isobutyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isobutyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isobutyl acetate, the person performing the operation should be informed of isobutyl acetate's hazardous properties.

• Any clothing which becomes wet with liquid isobutyl acetate should be removed immediately and not reworn until the isobutyl acetate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid isobutyl acetate may contact the eyes.

SANITATION

• Skin that becomes wet with liquid isobutyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any isobutyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isobutyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray application of varnishes and nitrocellulose lacquers as protective and finish coatings for wood, plastic, metal, leather, and other surfaces	Local exhaust ventilation; personal protective equipment
Liberation during application of varnishes and nitrocellulose lacquers as protective and finish coatings for wood, paper, metal, leather, and other surfaces by dipping, roller coating, tumbling, knifing, or brushing	Local exhaust ventilation; general dilution ventilation
Liberation during oven backing of phenolic and epoxy coatings	General dilution ventilation
Liberation during application of nitrocellulose, cellulose acetate, cellulose acetate butyrate, and cyclized rubber adhesives by machine spraying, dipping, roller coating, tumbling, knifing, or brushing in shoe manufacturing, book binding, packaging, leather processing, photographic film manufacturing, and paper processing	Local exhaust ventilation; general dilution ventilation
Use and liberation during manual application of nitrocellulose, cellulose acetate, cellulose acetate butyrate, and cyclized rubber adhesives	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during cleaning and maintenance of acetate-processing equipment, including kettles, distillation columns, and storage vessels	Personal protective equipment
Liberation during manufacture of some perfumes, cosmetics, and flavoring agents	General dilution ventilation
Liberation during spray application of vinyl-based primers, maintenance paints, and other industrial coatings	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 isobutyl acetate 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 isobutyl acetate gets on the skin, promptly flush the contaminated skin with water. If isobutyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of isobutyl acetate, 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 isobutyl acetate 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 isobutyl acetate 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. Isobutyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Isobutyl acetate 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: "Isobutyl Acetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR ISOBUTYL ACETATE

Condition	Minimum Respiratory Protection* Required Above 150 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.
7500 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 7500 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 Isobutyl Alcohol

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: $(CH_3)_2CHCH_2OH$
- Synonyms: Isobutanol; IBA; 2-methyl-1-propanol; isopropylcarbinol
- Appearance and odor: Colorless liquid with a mild, non-residual odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isobutyl alcohol is 100 parts of isobutyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 300 milligrams of isobutyl alcohol per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for isobutyl alcohol a Threshold Limit Value of 50 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isobutyl alcohol 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 isobutyl alcohol may cause irritation of the eyes, nose, and throat, headache, dizziness, and drowsiness.

2. Long-term Exposure: Drying and cracking of the skin may result from prolonged skin exposure.

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 isobutyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isobutyl alcohol 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 isobutyl alcohol exposure.

—Skin disease: Isobutyl alcohol 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 isobutyl alcohol 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 isobutyl alcohol 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 isobutyl alcohol 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**

Isobutyl alcohol vapor had a narcotic effect in high concentrations (6400 ppm) for mice, and was lethal at 10,000 to 15,000 ppm. In employees, repeated exposures at 100 ppm had no significant effect, although irritation of the eyes and throat were observed in other studies where the vapor concentrations were higher. Isobutyl alcohol is a mild skin irritant. 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.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74
2. Boiling point (760 mm Hg): 108 C (226 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of isobutyl alcohol): 2.6
5. Melting point: −108 C (−162 F)
6. Vapor pressure at 20 C (68 F): 8.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 8.7
8. Evaporation rate (butyl acetate = 1): 0.82

- **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 isobutyl alcohol.
4. Special precautions: Isobutyl alcohol will attack some forms of plastics, rubber, and coatings. It may react with metallic aluminum at high temperatures.

- **Flammability**

1. Flash point: 27.8 C (82 F) (closed cup)
2. Autoignition temperature: 427 C (800 F)
3. Flammable limits in air, % by volume (at 212 F): Lower: 1.2; Upper: 10.9
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Both Summer and May report an odor threshold of 40 ppm.
2. Eye Irritation Level: Patty states, "Fassett has studied isobutyl alcohol under the same conditions of exposure as for n-butyl alcohol. No evidence of eye irritation was noted with repeated 8-hour exposures to levels on the order of 100 ppm. Animal data showed that it was very similar to n-butyl alcohol in its effects." n-Butyl alcohol is known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of isobutyl alcohol is below the permissible exposure limit, 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 isobutyl alcohol 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 isobutyl alcohol may be used. An analytical method for isobutyl alcohol 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 isobutyl alcohol.
- Clothing wet with liquid isobutyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isobutyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isobutyl alcohol, the person performing the operation should be informed of isobutyl alcohol's hazardous properties.
- Any clothing which becomes wet with liquid isobutyl alcohol should be removed immediately and not reworn until the isobutyl alcohol is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid isobutyl alcohol may contact the eyes.

SANITATION

• Skin that becomes wet with liquid isobutyl alcohol should be promptly washed or showered to remove any isobutyl alcohol.
• Employees who handle liquid isobutyl alcohol should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isobutyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray applications of nitrocellulose lacquers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use of industrial cleaners; during use of paint removers	General dilution ventilation; personal protective equipment
Liberation during hand application of nitrocellulose lacquers; during manufacture of lubricating oil and hydraulic fluids; during manufacture of amino resins and plasticizers	General dilution ventilation
Use during manufacture of nitrocellulose lacquers, paint removers, and industrial cleaners	General dilution ventilation; personal protective equipment
Liberation during manufacture of acetaldehyde; during distillation of whiskey	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 isobutyl alcohol 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 isobutyl alcohol gets on the skin, promptly flush the contaminated skin with water. If isobutyl alcohol soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.
• **Breathing**
If a person breathes in large amounts of isobutyl alcohol, 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 isobutyl alcohol 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 isobutyl 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, 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. Isobutyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
• Waste disposal methods:
Isobutyl alcohol 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: "Isobutyl Alcohol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Isobutyl Alcohol*, New York, 1966.

RESPIRATORY PROTECTION FOR ISOBUTYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 100 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 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.

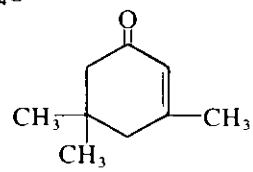
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ISOPHORONE

INTRODUCTION

This guideline summarizes pertinent information about isophorone 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:** $C_9H_{14}O$
- **Structure:**



- **Synonyms:** Isoacetophorone; isoforon; 3,5,5-trimethyl-2-cyclohexene-1-one
- **Identifiers:** CAS 78-59-1; RTECS GW7700000; DOT not assigned
- **Appearance and odor:** Colorless to pale yellow liquid with an odor like peppermint or camphor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 138.23
2. Boiling point (at 760 mmHg): 215°C (419°F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of isophorone): 4.77
5. Melting point: -8.1°C (17°F)
6. Vapor pressure at 20°C (68°F), 0.26 mmHg; at 25°C (77°F), 0.44 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 1.2
8. Evaporation rate (butyl acetate = 1): 0.03
9. Saturation concentration in air (approximate): At 20°C (68°F), 0.034% (340 ppm); at 25°C (77°F), 0.06% (600 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving isophorone.
3. Caution: Isophorone will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 84.4°C (184°F) (closed cup)
2. Autoignition temperature: 460°C (860°F)
3. Flammable limits in air, % by volume: Lower, 0.8; upper, 3.8
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.2 ppm
2. Eye irritation level: 25 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, isophorone 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 isophorone is 25 parts of isophorone per million parts of air (ppm) [140 milligrams of isophorone per cubic meter of air (mg/m³)] as a time-weighted average (TWA) over an 8-hour workshift. The NIOSH REL is 4 ppm (23 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 ceiling (TLV®-C), the concentration that should not be exceeded during any part of the working exposure, is 5 ppm (25 mg/m³) (Table 1).

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Table 1.—Occupational exposure limits for isophorone

	Exposure limits ppm	mg/m³
OSHA PEL TWA	25	140
NIOSH REL TWA	4	23
ACGIH TLV®-ceiling	5	25

HEALTH HAZARD INFORMATION

• **Routes of exposure**

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

• **Summary of toxicology**

Effects on animals: Acute inhalation of isophorone by rats caused narcosis and death. Subchronic inhalation of isophorone by guinea pigs and rats caused injury to the kidneys (congestion, dilated Bowman's capsules, or cloudy swelling of convoluted tubules) and lungs (congestion, hemorrhage, desquamation, or pneumonia).

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to isophorone can cause depressed appetite and body weight, headache, dizziness, fatigue, nausea, and diarrhea. Irritation of the skin, eyes, and upper and lower respiratory tracts can also occur.
2. *Long-term (chronic):* Exposure to isophorone can cause drying, 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 isophorone, 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 isophorone 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, concurrent dermatitis, and significant breathing impairment due to preexisting 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 frequent examinations may be necessary should a worker develop symptoms that may be attributed to exposure to isophorone. 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 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.

• **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 isophorone 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 isophorone vapors with a charcoal tube followed by desorption with carbon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure isophorone may also be used if available. A detailed sampling and analytical method for isophorone may be found in the *NIOSH Manual of Analytical Methods* (method number 2508).

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 isophorone.

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

SANITATION

Clothing which is contaminated with isophorone 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 isophorone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of isophorone's hazardous properties.

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

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

Workers who handle isophorone 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 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 isophorone 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 isophorone 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 isophorone

Operations	Controls
During use as a solvent in the manufacture of vinyl resins, nitrocellulose, fats, chlorinated rubber, herbicides, coatings, roll-coating finishes, siding, paint, adhesives, and inks	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use in organic synthesis in the manufacture of lubricating oil additives, fungicides, and tetramethylquanidine	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 isophorone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If isophorone 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 isophorone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If isophorone gets on the skin, wash it immediately with soap and water. If isophorone 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 isophorone 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 isophorone, 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 isophorone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing isophorone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Isophorone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing isophorone 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 isophorone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 40 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 100 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 200 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
	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 supplied air respirator with a tight-fitting facepiece and operated in a continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 800 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 800 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 4 ppm (23 mg/m^3) (TWA).

Occupational Health Guideline for Isopropyl Acetate

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: $CH_3COOCH(CH_3)_2$
- Synonyms: Isopropyl ester of acetic acid; sec-propyl acetate
- Appearance and odor: Colorless liquid with a fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isopropyl acetate is 250 parts of isopropyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 950 milligrams of isopropyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isopropyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to isopropyl acetate may cause irritation of the eyes, nose, and throat. Severe overexposure may cause weakness, drowsiness, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure may produce 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 isopropyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isopropyl acetate 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 isopropyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isopropyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Isopropyl acetate 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 isopropyl acetate 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 isopropyl acetate 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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Isopropyl acetate irritates the eyes and upper respiratory tract. It may produce narcosis at high concentrations approaching the lethal level in animals. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 102
  2. Boiling point (760 mm Hg): 90 C (194 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.

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

3. Specific gravity (water = 1): 0.87

4. Vapor density (air = 1 at boiling point of isopropyl acetate): 3.5

5. Melting point: −69 C (−92 F)

6. Vapor pressure at 20 C (68 F): 43 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 2.9

8. Evaporation rate (butyl acetate = 1): 5

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with nitrates, strong oxidizers, strong alkalies, or 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 isopropyl acetate.

4. Special precautions: Isopropyl acetate will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 4.4 C (40 F) (closed cup)

2. Autoignition temperature: 460 C (860 F)

3. Flammable limits in air, % by volume: Lower: 1.8; Upper: 8.0

4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

• **Warning properties**

1. Odor Threshold: May reports two odor thresholds for isopropyl acetate: 30 ppm and 400 ppm.

2. Eye Irritation Level: Patty reports that 200 ppm causes eye irritation in man.

3. Evaluation of Warning Properties: Because of its low thresholds of odor and eye irritation, isopropyl acetate 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 isopropyl acetate 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 isopropyl acetate may be used. An analytical method for isopropyl acetate 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 isopropyl acetate.

• Clothing wet with liquid isopropyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isopropyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isopropyl acetate, the person performing the operation should be informed of isopropyl acetate's hazardous properties.

• Any clothing which becomes wet with liquid isopropyl acetate should be removed immediately and not reworn until the isopropyl acetate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid isopropyl acetate may contact the eyes.

SANITATION

• Skin that becomes wet with liquid isopropyl acetate should be promptly washed or showered with soap or mild detergent and water to remove any isopropyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isopropyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during coating application to artificial silk, leather, and vinyl resin fabrics	Local exhaust ventilation; general dilution ventilation
Liberation during use as a vehicle solvent during spray application of cellulose nitrate and ethyl cellulose lacquers	Local exhaust ventilation; spray booths; personal protective equipment
Liberation during manufacture of cellulose nitrate and ethyl cellulose lacquers and thinners	Local exhaust ventilation; general dilution ventilation
Use as a solvent of synthetic resins in plastics industry	Local exhaust ventilation; general dilution ventilation
Liberation during manufacture and use of printing and litho inks; during manufacture of perfumes and flavoring agents	Local exhaust ventilation; general dilution ventilation
Use as a general solvent for waxes, gums, and oils	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis	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 isopropyl acetate 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 isopropyl acetate gets on the skin, promptly flush the contaminated skin with water. If isopropyl acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of isopropyl acetate, 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 isopropyl acetate 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 isopropyl acetate 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. Isopropyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Isopropyl acetate 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.

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RESPIRATORY PROTECTION FOR ISOPROPYL ACETATE

Condition	Minimum Respiratory Protection* Required Above 250 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.
12,500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
16,000 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 16,000 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 Isopropyl Alcohol

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: $CH_3CHOHCH_3$
- Synonyms: Isopropanol; IPA; 2-propanol; sec-propyl alcohol
- Appearance and odor: Colorless liquid with an odor of rubbing alcohol.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isopropyl alcohol is 400 parts of isopropyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 980 milligrams of isopropyl alcohol per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 400 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 800 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Isopropyl Alcohol should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isopropyl alcohol 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: Exposure to high air concentrations of isopropyl alcohol may cause mild irritation of the eyes, nose, and throat. Drowsiness, headache, and incoordination may also occur. Swallowing isopropyl alcohol may cause drowsiness, unconsciousness, and death. Gastrointestinal pain, cramps, nausea, vomiting, and diarrhea may also result from swallowing this alcohol.

2. Long-term Exposure: Drying and cracking of the skin may result from prolonged skin exposure. Epidemiological investigations have established that a carcinogenic substance is present in isopropyl alcohol manufacturing areas, but have not confirmed isopropyl alcohol as a causative agent of cancer.

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 isopropyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isopropyl alcohol 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, and respiratory system should be stressed.

—Skin disease: Isopropyl alcohol 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 isopropyl alcohol 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 isopropyl alcohol 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 isopropyl

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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alcohol might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

The most important toxic effect of isopropyl alcohol is narcosis, which occurs in mice at vapor concentrations of 3000 ppm, the effects increasing with the duration of exposure. Exposure to higher concentrations results in ataxia, followed by deep narcosis and death. Reversible changes occurred in the liver fat of mice repeatedly exposed to high concentrations of vapor. Isopropyl alcohol is metabolized fairly rapidly, and acetone may be detected in the urine following heavy exposures. Human volunteers reported mild irritation of the eyes, nose, and throat after 3 to 5 minutes exposure to vapor at 400 ppm; at 800 ppm the results were not severe, but most subjects found the atmosphere to be objectionable. Accidental, extensive wetting of the skin could occur in industrial situations and as isopropyl alcohol is absorbed readily through the skin, the additive effect of inhalation and skin absorption could have serious results. Similarly, there is a risk of deliberate ingestion of isopropyl alcohol as a substitute for ethyl alcohol, which would add to the effects of inhalation. The defatting action of isopropyl alcohol can cause mild skin irritation, but a small percentage of workers may develop contact dermatitis of a more serious nature. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 60
2. Boiling point (760 mm Hg): 82 C (180 F)
3. Specific gravity (water = 1): 0.78
4. Vapor density (air = 1 at boiling point of isopropyl alcohol): 2.1
5. Melting point: −89 C (−128 F)
6. Vapor pressure at 20 C (68 F): 33 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): 2.83

• **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 isopropyl alcohol.
4. Special precautions: Isopropyl alcohol will attack some forms of plastics, rubber, and coatings. It may also react with metallic aluminum at high temperatures.

• **Flammability**

1. Flash point: 12 C (53 F) (closed cup)
2. Autoignition temperature: 399 C (750 F)
3. Flammable limits in air, % by volume: Lower: 2.0; Upper: 12.0
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

• **Warning properties**

1. Odor Threshold: Patty reports, "Scherberger et al. stated that the concentration with identifiable odor of isopropyl alcohol is 200 ppm." May reports an odor threshold of 45 ppm.
2. Irritation Level: According to Patty, "mild irritation of the eyes, nose, and throat was induced in human subjects exposed by Nelson and associates for 3 to 5 minutes to 400 ppm of isopropyl alcohol."
3. Evaluation of Warning Properties: Through its odor and irritant effects, isopropyl alcohol can be detected below or at the permissible exposure limit. For the purposes of this guideline, therefore, it is treated as a material with adequate 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 isopropyl alcohol. 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 isopropyl alcohol vapors using an adsorption tube with subsequent desorption with 2-butanol 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 isopropyl alcohol may be used. An analytical method for isopropyl alcohol 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 isopropyl alcohol.
- Any clothing which becomes wet with liquid isopropyl alcohol should be removed immediately and not reworn until the isopropyl alcohol is removed from the clothing.
- Clothing wet with liquid isopropyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isopropyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isopropyl alcohol, the person performing the operation should be informed of isopropyl alcohol's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid isopropyl alcohol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid isopropyl alcohol should be promptly washed or showered to remove any isopropyl alcohol.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isopropyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in spray and heat applications of surface coatings, including stain, varnish, nitrocellulose lacquers, and quick-drying inks and paints	General dilution ventilation; personal protective equipment
Use as a solvent in application other than spray or heat of surface coatings, including stain, varnish, nitrocellulose lacquers, quick-drying inks and paints, textile coatings and dyes, dopes, and polishes	General dilution ventilation; personal protective equipment
Use in manufacture and liberation during packing of acetone	General dilution ventilation; personal protective equipment
Use as a solvent in manufacture of surface coatings and thinners	General dilution ventilation; personal protective equipment
Use in organic synthesis for isopropyl derivatives, including phenols, acetates, xanthates, ether, amines, myristate, palmitate, nitrite, and glycerin	General dilution ventilation; personal protective equipment
Use in manufacture of cosmetics, including liniments, skin lotions, permanent wave lotions, and color hair rinses	General dilution ventilation; personal protective equipment
Liberation during use as a disinfectant and sanitizer; use during cleaning and degreasing operations	General dilution ventilation; personal protective equipment
Use in preparation, manufacture, and packaging of disinfectants and sanitizers, including rubbing alcohol, other antiseptic solutions, skin astringents, mouth washes, and medicated sprays	General dilution ventilation; personal protective equipment

Operation	Controls
Use in manufacture of cleaning and degreasing agents, including stain and spot removers, glass cleaners, rug and uphostery cleaning, tar remover, liquid soap, and windshield cleaner fluid; use in manufacture of de-icing, de-fogging, and anti-freeze products	General dilution ventilation; personal protective equipment
Use in extraction and purification of alkaloids, proteins, chlorophyll, perfumes, sulfuric acid, vitamins, kelp, pectin, resins, gums, and waxes	General dilution ventilation; personal protective equipment
Use in manufacture of rubber products; use as an additive in anti-stalling gasoline, lubricants, denatured ethyl alcohol, hydraulic brake fluids, and rocket fuel	General dilution ventilation; personal protective equipment
Use in manufacture of adhesives, including nitrocellulose film and microfilm cement; use in manufacture of safety glass	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 isopropyl alcohol 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 isopropyl alcohol gets on the skin, flush the contaminated skin with water. If isopropyl alcohol soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of isopropyl alcohol, 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 isopropyl alcohol 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 isopropyl 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, 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. Isopropyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Isopropyl alcohol 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: "Isopropyl Alcohol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• American Industrial Hygiene Association: "Propanol," *Hygienic Guide Series*, Detroit, Michigan, 1961.

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RESPIRATORY PROTECTION FOR ISOPROPYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 400 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.
20,000 ppm or less	A gas mask with 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 20,000 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 Isopropylamine

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: $(CH_3)_2CHNH_2$
- Synonyms: Monoisopropylamine; 2-aminopropane
- Appearance and odor: Colorless liquid with a pungent, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isopropylamine is 5 parts of isopropylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 12 milligrams of isopropylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isopropylamine 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**

1. Short-term Exposure: Isopropylamine vapor may cause irritation of the nose, throat, and lungs. Both isopropylamine liquid and vapor may cause irritation or burning of the eyes and skin. Permanent eye damage may occur if proper care is not given immediately. Breathing difficulties may occur either immediately or may be delayed.

2. Long-term Exposure: Repeated or prolonged exposure to isopropylamine causes an 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 isopropylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isopropylamine 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 isopropylamine exposure.

—Chronic respiratory disease: Isopropylamine causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isopropylamine might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: Isopropylamine is an eye irritant and has caused corneal edema in workers. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Skin disease: Isopropylamine 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**

Isopropylamine vapor is a respiratory and eye irritant. Rats exposed to 8000 ppm for 4 hours died as a result of pulmonary edema. Human subjects experienced irritation of the nose and throat after brief exposures to 10 to 20 ppm. Workers complained of transient visual disturbances after exposure to the vapor for 8 hours, probably due to mild corneal edema that usually cleared within 3 or 4 hours. The liquid is capable of causing very severe eye burns, which may cause permanent visual impairment. Isopropylamine in both liquid and vapor forms is irritating to the skin and may cause skin burns; repeated lesser exposures may result in dermatitis.

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: 59.1
  2. Boiling point (760 mm Hg): 32.4 C (90 F)
  3. Specific gravity (water = 1): 0.68
  4. Vapor density (air = 1 at boiling point of isopropylamine): 2.03
  5. Melting point: −95 C (−139 F)
  6. Vapor pressure at 20 C (68 F): 478 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): Greater than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact of liquid isopropylamine with strong acids will cause explosive spattering. 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 in a fire involving isopropylamine.
  4. Special precautions: Liquid isopropylamine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −37 C (−35 F) (closed cup)
  2. Autoignition temperature: 402 C (756 F).
  3. Flammable limits in air, % by volume: Lower: 2.0; Upper: 10.4
  4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical
- **Warning properties**
  1. Odor Threshold: Patty reports that at a concentration of 5 to 10 ppm, the ammoniacal odor is definite, and at 10 to 20 ppm, the odor is strong.
  2. Eye Irritation Level: The MCA Chemical Safety Data Sheet notes that the vapors of isopropylamine are highly irritating to the eyes, but no quantitative information is available concerning the threshold of eye irritation.
  3. Other Information: Patty reports that nose and throat irritation results from short exposures to 10 to 20 ppm isopropylamine. No eye irritation is cited.
  4. Evaluation of Warning Properties: Since the odor of isopropylamine is definite at a concentration which is only twice the permissible exposure, and since nose and throat irritation occurs at a concentration which is only 2 to 4 times the permissible exposure, isopropylamine 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 isopropylamine in a bubbler containing sulfuric acid, followed by treatment with sodium hydroxide, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure isopropylamine may be used. An analytical method for isopropylamine 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 isopropylamine, where skin contact may occur.
- Clothing wet with liquid isopropylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isopropylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isopropylamine, the person performing the operation should be informed of isopropylamine's hazardous properties.
- Where exposure of an employee's body to liquid isopropylamine may occur, facilities for quick drench-

ing of the body should be provided within the immediate work area for emergency use.

- Any clothing which becomes wet with isopropylamine or non-impervious clothing which becomes contaminated with isopropylamine should be removed immediately and not reworn until the isopropylamine 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 isopropylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid isopropylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid isopropylamine should be immediately washed or showered to remove any isopropylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isopropylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use as an intermediate in synthesis of agricultural chemicals	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solubilizer for 2,4-D and 2,4,5-T herbicides in hard water	Local exhaust ventilation; personal protective equipment
Use as an intermediate in synthesis of insecticides and bactericides	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use with surface-active sulfonate to form oil-soluble emulsifier and detergent for use in dry cleaning operations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an intermediate in synthesis of vulcanization accelerators for sulfur-cured rubbers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of ore flotation agents; use as a depilatory on skins and hides in leather manufacture; use in manufacture of emulsion-type floor polish	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a general solvent; use as a stabilizer against oxidation and polymerization	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of medicinals in purification of penicillin and streptomycin; use as an intermediate in synthesis of some dyes	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 isopropylamine 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 isopropylamine gets on the skin, immediately flush the contaminated skin with water. If isopropylamine soaks 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 isopropylamine, 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 isopropylamine has 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 or leaks until cleanup has been completed.

• If isopropylamine 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. Isopropylamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Isopropylamine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Isopropylamine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• Patty, F. A. (ed.): *Toxicology,* Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Isopropylamine,* New York, 1971.

RESPIRATORY PROTECTION FOR ISOPROPYLAMINE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
250 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) providing protection against isopropylamine. A gas mask with a chin-style or a front- or back-mounted canister which provides protection against isopropylamine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
4000 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 4000 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 isopropylamine. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Isopropylether

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: $((CH_3)_2CH)_2O$
- Synonyms: Diisopropyl ether; 2-isopropoxypropane
- Appearance and odor: Colorless liquid with a sharp, sweet, ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for isopropylether is 500 parts of isopropylether per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2100 milligrams of isopropylether per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for isopropylether a Threshold Limit Value of 250 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Isopropylether 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: Strong concentrations of isopropylether vapors may cause irritation of the eyes and nose. Animal experiments suggest that exposure to high concentrations of this chemical may cause drowsiness, dizziness, and unconsciousness.

2. Long-term Exposure: Repeated or prolonged exposure to liquid isopropylether may cause dryness and 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 isopropylether.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to isopropylether 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 isopropylether exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of isopropylether might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Isopropylether 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**

Isopropylether vapor is a mild irritant of the eyes and mucous membranes; high levels cause narcosis in animals. Animals exposed to 30,000 ppm for 1 hour showed signs of narcosis. Exposure of human subjects to 800 ppm for 5 minutes caused irritation of the eyes and nose and some reported respiratory discomfort; exposure to 500 ppm for 15 minutes was not irritating, but at 300 ppm one third of the subjects objected to the unpleasant odor. The liquid dropped in the eye of a rabbit caused minor injury. In rabbits, repeated skin exposure to the liquid for 10 days caused dermatitis, possibly due to defatting action.

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

September 1978

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.2
2. Boiling point (760 mm Hg): 68.9 C (156 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of isopropylether): 3.5
5. Melting point: −85 C (−121 F)
6. Vapor pressure at 20 C (68 F): 119 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): 8

- **Reactivity**

1. Conditions contributing to instability: Contact with air causes formation of explosive peroxides that may detonate when heated or subjected to shock.
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 isopropylether.
4. Special precautions: Isopropylether will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −27.8 C (−18 F) (closed cup)
2. Autoignition temperature: 443 C (830 F)
3. Flammable limits in air, % by volume: Lower: 1.4; Upper: 7.9
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states that 35% of human subjects exposed experimentally to isopropylether "objected to the unpleasant odor of this solvent at a vapor concentration of 300 ppm."
2. Irritation Level: Patty states that "Silverman et al. reported that humans exposed to a vapor concentration of 500 ppm isopropyl ether for 15 minutes while watching a movie noted no irritating properties . . . . At 800 ppm for 5 minutes most subjects reported irritation of the eyes and nose, and the most sensitive reported respiratory discomfort."
3. Evaluation of Warning Properties: Through its odor and irritant effects, isopropylether can be detected at or slightly above the permissible exposure limit. For the purposes of this guideline, therefore, isopropylether 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 isopropylether may be used. An analytical method for isopropylether 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 isopropylether.

• Clothing wet with isopropylether should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of isopropylether from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the isopropylether, the person performing the operation should be informed of isopropylether's hazardous properties.

• Any clothing which becomes wet with liquid isopropylether should be removed immediately and not reworn until the isopropylether is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid isopropylether may contact the eyes.

SANITATION

• Skin that becomes wet with liquid isopropylether should be promptly washed or showered with soap or mild detergent and water to remove any isopropylether.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to isopropylether may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in extraction processes, rubber adhesives, lacquers, resins, oils, cellulose, pharmaceutical manufacture, smokeless gunpowder, and textile spot cleaning	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis as an alkylation agent; emulsion breaker in petroleum industry; and as blending agent for gasoline	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 isopropylether 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 isopropylether gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid isopropylether soaks 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 isopropylether, 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 isopropylether 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 isopropylether 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. Isopropylether 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 isopropylether vapors are permitted.

• Waste disposal method:

Isopropylether may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR ISOPROPYLETHER

Condition	Minimum Respiratory Protection* Required Above 500 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 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.

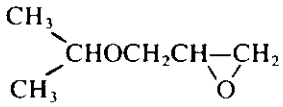
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ISOPROPYL GLYCIDYL ETHER

INTRODUCTION

This guideline summarizes pertinent information about isopropyl glycidyl ether (IGE) 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:**



- **Synonyms:** 1,2-epoxy-3-isopropoxypropane; glycidyl isopropyl ether; IGE; (isopropoxymethyl)oxirane; isopropyl epoxypropyl ether
- **Identifiers:** CAS 4016-14-2; RTECS TZ3500000; DOT not assigned
- **Appearance:** Colorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 116.18
2. Boiling point (at 760 mmHg): 137 °C (270 °F)
3. Specific gravity (water = 1): 0.9
4. Vapor density (air = 1 at boiling point of IGE): 4.0
5. Vapor pressure at 25 °C (77 °F): 9.4 mmHg
6. Solubility in water, g/100 g water at 20 °C (68 °F): 18.8
7. Evaporation rate (butyl acetate = 1): 0.99
8. Saturation concentration in air (approximate) at 25 °C (77 °F): 1.237% (12.370 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with strong caustics may cause polymerization. IGE should not be exposed to air or light 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 IGE.
3. Caution: IGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 33 °C (92 °F) (closed cup)
2. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
3. Class IC Flammable 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, IGE should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for IGE is 50 parts of IGE per million parts of air (ppm) [240 milligrams of IGE 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) is 50 ppm (240 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®) is 50 ppm (240 mg/m^3) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 75 ppm (360 mg/m^3) (Table 1).

Table 1.—Occupational exposure limits for isopropyl glycidyl ether

	Exposure limits ppm	Exposure limits mg/m^3
OSHA PEL TWA	50	240
NIOSH REL ceiling (15 min)	50	240
ACGIH TLV® TWA	50	240
STEL	75	360

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Division of Standards Development and Technology Transfer

HEALTH HAZARD INFORMATION

• **Routes of exposure**
IGE 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 IGE to mice, rats, and rabbits caused central nervous system depression. Subchronic inhalation of IGE by rats caused decreased weight gain, inflammation of the lungs, pneumonia, and respiratory distress.

• **Signs and symptoms of exposure**
1. *Short-term (acute):* Exposure to IGE can cause mental confusion and moderate irritation of the eyes, skin, and respiratory tract.
2. *Long-term (chronic):* Exposure to IGE can cause dermatitis and skin sensitization.

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 IGE, 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 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 IGE 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 IGE. 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 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

• **Ceiling concentration evaluation**
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of IGE. 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 IGE vapors with charcoal tubes followed by desorption with car-

bon disulfide and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure IGE may also be used if available. A detailed sampling and analytical method for IGE may be found in the *NIOSH Manual of Analytical Methods* (method number S77).

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 IGE.

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

SANITATION

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

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

Skin that becomes contaminated with IGE 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 of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle IGE 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 IGE 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 isopropyl glycidyl ether

Operations	Controls
During use as a reactive diluent for epoxy resins; during use as a chemical intermediate for the synthesis of esters and ethers	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 IGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

If IGE 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 IGE, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If IGE gets on the skin, wash it immediately with soap and water. If IGE 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 IGE 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 IGE, 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 IGE vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing IGE may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. IGE should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing IGE 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 flash back 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 isopropyl glycidyl ether

Condition	Minimum respiratory protection*†
Concentration:	
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 1,500 ppm	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 1,500 ppm	Any self-contained breathing apparatus with a full facepiece and operated in 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) (ceiling).

Occupational Health Guideline for Ketene

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_2CO
- Synonyms: None
- Appearance and odor: Colorless gas with a sharp odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ketene is 0.5 parts of ketene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.9 milligrams of ketene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ketene can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ketene may cause irritation of the eyes, nose, throat, and lungs. It may also cause cough, chest pain, and severe breathing difficulty. This may occur several hours after exposure and may be severe enough to cause death.

2. Long-term Exposure: Chronic overexposure to ketene may cause permanent lung damage.

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 ketene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ketene 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: Ketene causes lung damage in animals.

—FVC and FEV (1 sec): Ketene is a severe pulmonary irritant in animals.

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.

- **Summary of toxicology**

Ketene is a severe respiratory irritant. Concentrations over 100 ppm were invariably fatal to mice, rats, and guinea pigs; death occurred rapidly with symptoms of marked eye, nose, throat, and pulmonary irritation; autopsies showed major damage to alveolar walls with pulmonary edema. The LC50 for mice was established at 17 ppm for 10 minutes, but 1 ppm was tolerated without apparent chronic injury by several animal species exposed for 6 hours daily for 6 months. Although it has not been reported in humans, animal data indicate that chronic pulmonary changes (emphysema and fibrosis) may result from repeated acute exposures.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 42
  2. Boiling point (760 mm Hg): −56 C (−69 F)
  3. Specific gravity (water = 1): Not applicable

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. Vapor density (air = 1 at boiling point of ketene): 1.45

5. Melting point: −151 C (−239 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 with water to form acetic acid

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Ketene reacts vigorously with water and with a wide variety of organic compounds.

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

4. Special precautions: Dimerization of ketene to diketene occurs even at low temperatures.

• **Flammability**

1. Flash point: Not applicable (gas)

2. Autoignition temperature: Data not available

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

4. Extinguishant: Stop flow of gas

• **Warning properties**

1. Odor Threshold: No quantitative information is available.

2. Eye Irritation Level: Grant states that "exposure of monkeys to 23 ppm in air for 4 hours caused the animals to rub their eyes, cough, and become lethargic. . . . The dimer, diketene, is said to be lacrimatory and to cause marked irritation of the conjunctiva."

3. Evaluation of Warning Properties: Since there is no quantitative information relating its warning properties to air concentrations, ketene 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 ketene in a bubbler containing alkaline hydroxlammonium chloride, followed by treatment with ferric chloride, and colorimetric analysis. An analytical method for ketene 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.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ketene may occur and control methods which may be effective in each case:

Operation	Controls
Use as an intermediate in production of acetic anhydride, cellulose and vinyl acetate resins and plastics, acrylic resins, dyes, pigments, and pharmaceuticals	Process enclosure; local exhaust ventilation; personal protective equipment
Use in industrial organic synthesis in manufacture of acetyl chloride, acid anhydrides, esters, nitriles, and diketene	Process enclosure; local exhaust ventilation; personal protective equipment
Use during laboratory operations as an acetylating agent	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 ketene, move the exposed person to fresh air at once. If breathing is difficult, properly trained personnel may assist the affected person by administering oxygen. 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 AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If ketene is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas.

• Waste disposal method:

Ketene may be disposed of by burning at a safe location or in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR KETENE

Condition	Minimum Respiratory Protection* Required Above 0.5 ppm
Vapor Concentration	
25 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 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 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 INORGANIC LEAD

INTRODUCTION

"Inorganic lead" is defined as lead oxides, metallic lead, and lead salts (including organic salts such as lead soaps but excluding lead arsenate). This guideline summarizes pertinent information about inorganic lead 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:** Pb
- **Synonyms:** C.I. pigment metal 4, C.I. 77575, KS-4, lead flake, lead S2
- **Identifiers:** CAS 7439-92-1; RTECS OF7525000; DOT 1794
- **Appearance and odor:** Bluish-white, silvery, or gray odorless solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 207.19
2. Boiling point (at 760 mmHg): 1,740°C (3,164°F)
3. Specific gravity (water = 1): 11.34
4. Melting point: 327.5°C (621.5°F)
5. Insoluble in water

- **Reactivity**

1. Incompatibilities: Lead reacts vigorously with oxidizing materials. Contact with hydrogen peroxide or active metals such as sodium or potassium may cause fires or explosions.
2. Hazardous decomposition products: Toxic fumes (e.g., lead oxide) may be released in a fire involving inorganic lead.

- **Flammability**

1. Extinguishant: Dry sand, dry dolomite, or dry graphite
2. Caution: Lead is combustible in powder form when exposed to heat or flame

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, inorganic lead should be treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for inorganic lead is 50 micrograms of lead per cubic meter of air ($\mu g/m^3$) as a time-weighted average (TWA) concentration over an 8-hour workshift. If a worker is exposed to lead for more than 8 hours in any workday, the PEL, as a TWA for that day, shall be reduced according to the following formula: maximum permissible limit (in $\mu g/m^3$) = 400 divided by hours worked in the day. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 100 $\mu g/m^3$ as a TWA for up to a 10-hour workshift, 40-hr. workweek. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.15 mg/m^3 (150 $\mu g/m^3$) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for inorganic lead

	Exposure units $\mu g/m^3$
OSHA PEL TWA	50
NIOSH REL TWA	100*
ACGIH TLV® TWA	150

* Air level to be maintained such that worker blood lead remains ≤60 $\mu g/100g$.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Inorganic lead may cause adverse health effects following exposure via inhalation or ingestion.

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• **Summary of toxicology**

1. *Effects on animals:* In rats or mice, chronic oral administration or subcutaneous or intraperitoneal injection of lead subacetate, lead acetate, or lead phosphate produced cancer of the kidneys. Intravenous or intraperitoneal injection of lead nitrate, lead acetate, or lead chloride to pregnant mice, rats, or hamsters caused increased fetal mortality and malformations of the posterior extremities and urogenital and intestinal tracts in the offspring.

2. *Effects on humans:* Inhalation or ingestion of inorganic lead has caused peripheral neuropathy with paralysis of the muscles of the wrists and ankles, encephalopathy, anemia (due to decreased red blood cell life and impaired heme synthesis), proximal kidney tubule damage, decreased kidney function, and chronic kidney disease. Lead can accumulate in the soft tissues and bones, with the highest accumulation in the liver and kidneys, and elimination is slow. Lead can penetrate the placental barrier, resulting in neurologic disorders in infants.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to inorganic lead can cause decreased appetite, insomnia, headache, muscle and joint pain, colic, and constipation.

2. *Long-term (chronic):* Exposure to inorganic lead can cause weakness, weight loss, nausea, vomiting, constipation, blue or blue-black dot-like pigmentation on the gums ("lead line"), severe headache and abdominal cramps, delirium, convulsions, 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 inorganic lead, 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 t[redacted] anticipated occupational risks. These should concentrate [redacted] the function and integrity of the kidneys and the hematopoietic (blood cell forming), nervous, gastrointestinal, and reproductive 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 inorganic lead 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 neuromuscular disease. In addition to the medical interview and physical examination, the physician should consider obtaining additional baseline electrophysiologic and electromyographic studies and an assessment of fertility, using standardized methods and evaluation criteria. The physician should also obtain baseline values for the complete blood count including the reticulocyte count and for those tests which characterize prior internal exposure (e.g., blood lead level) and the effects of prior exposures (e.g., erythrocyte zinc protoporphyrin and delta-aminolevulinic acid dehydrogenase).

• **Periodic medical screening and/or biologic monitori[redacted]**

Occupational health interviews and physical examinati[redacted] should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to inorganic lead. 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 kidneys and the hematopoietic (blood cell forming), nervous, gastrointestinal, 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 epidemiologic procedures and evaluation criteria: a complete blood count with reticulocyte count and those tests which characterize prior internal exposure (e.g., blood lead level) and the effects of exposures (e.g., erythrocyte zinc protoporphyrin and delta-aminolevulinic acid dehydrogenase).

• **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. Becau[redacted] occupational exposure to inorganic lead may cause adv[redacted] 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: Acute renal failure.
2. Delayed-onset or reproductive SHE's include: Inflammatory and toxic neuropathy and chronic renal failure.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to inorganic lead 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 inorganic lead with cellulose membrane filters followed by acid digestion and analysis by atomic absorption. A detailed sampling and analytical method for inorganic lead may be found in the *NIOSH Manual of Analytical Methods* (method number 7082).

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 inorganic lead.

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

SANITATION

Clothing which is contaminated with inorganic lead 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 inorganic lead from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of inorganic lead's hazardous properties.

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

Skin that becomes contaminated with inorganic lead 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 inorganic lead 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 lead 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 inorganic lead

Operations	Controls
During primary (ore) and secondary (scrap) smelting of lead; during the manufacture of storage batteries; during typecasting and remelting of type metal in printing	Process enclosure, local exhaust ventilation, dust control, personal protective equipment
During soldering in the fabrication of metal articles	Process enclosure, local exhaust ventilation, personal protective equipment
During melting and pouring of lead and alloys containing lead; during welding, burning, and cutting of metal structures containing lead or painted with lead containing surface coatings	Local exhaust ventilation, personal protective equipment
During the use of lead in the manufacture of surface coatings, including paints and varnishes; during the manufacture of ceramics and glass	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 inorganic lead, an eye-wash fountain should be provided within the immediate work area for emergency use.

If inorganic lead 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 compound.

• **Skin exposure**

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

If inorganic lead gets on the skin, wash it immediately with soap and water. If inorganic lead 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 inorganic lead 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 inorganic lead, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing inorganic lead may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. If in solid form, inorganic lead may be collected and placed in an appropriate container.
6. Inorganic lead 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 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 respirator 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 inorganic lead

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.5 mg/m³	Any supplied air respirator
	Any air-purifying respirator with a high-efficiency particulate filter
	Any self-contained breathing apparatus
Less than or equal to 1.25 mg/m³	Any powered air-purifying respirator with a high-efficiency particulate filter
	Any supplied-air respirator operated in a continuous flow mode
Less than or equal to 2.5 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
	Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Less than or equal to 50 mg/m³	Any supplied-air respirator with a half-mask and operated in a pressure-demand or other positive pressure mode
Less than or equal to 100 mg/m³	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 100 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 100 μg/m³ (TWA).

Occupational Health Guideline for Lindane*

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: $C_6H_6Cl_6$
- Synonyms: 1,2,3,4,5,6-Hexachlorocyclohexane; gamma-hexachlorocyclohexane; benzene hexachloride
- Appearance and odor: Colorless solid with a musty odor (pure material is odorless).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for lindane is 0.5 milligram of lindane per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Lindane 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 lindane may cause vomiting, restlessness, muscle spasms, convulsions, and respiratory failure. It may also cause severe breathing difficulties which may be delayed in onset. Exposure to lindane vapors may cause headache, vomiting, and irritation of the eyes, nose, and throat. Repeated exposure to lindane may cause severe blood disorders which may be fatal. Skin rash may also occur from exposure to 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 lindane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to lindane 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 eyes, central nervous system, blood, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Lindane may cause aplastic anemia. A complete blood count should be performed, including a red cell count, a white cell count, and a differential count of a stained smear, as well as hemoglobin and hematocrit. The concentration of lindane in the blood is an indication of the extent of absorption.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Lindane (the gamma isomer of hexachlorocyclohexane) dust or vapor is a convulsant and causes cancer in mice. Repeated feeding to rats of 800 ppm in the diet resulted in mild liver damage; kidney damage occurred at higher levels. Mice fed 400 ppm in the diet developed liver tumors and, in some cases, lung metastases. In humans, accidental ingestion has caused fatalities; effects were repeated, violent, clonic convulsions, sometimes superimposed on a continuous tonic spasm; respiratory difficulty and cyanosis secondary to the convulsions were common. Exposure to the vapor causes irritation of the eyes, nose, and throat, severe headache, and nausea. Lindane levels in the blood do not appear to increase with increased duration of exposure but primarily reflect recent lindane absorption; production workers

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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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exposed to air levels of 31 to 1800 ug/m³ had blood levels of 1.9 to 8.3 ppb. Lindane has been suspected as a cause of aplastic anemia in a number of cases reported from various countries; this condition may have been caused either by a contaminant, or a thermal breakdown product of lindane, because many of the cases were associated with a space vaporizer as the source of exposure. The dry material applied to the skin of rabbits caused moderate skin irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 290.8
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 1.89
  4. Vapor density (air = 1 at boiling point of lindane): Not applicable
  5. Melting point: 112 C (234 F)
  6. Vapor pressure at 20 C (68 F): 0.0000094 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.001
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: Above 177 C (350 F) lindane decomposes to form toxic and irritating hydrogen chloride gas.
  2. Incompatibilities: None
  3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, hydrogen chloride, and carbon monoxide) may be released in a fire involving lindane.
  4. Special precautions: None
- **Flammability**
  1. Not combustible, but may be dissolved in a combustible solvent
- **Warning properties**

Since the vapor pressure is so low, warning properties are not considered.

Grant states that "as a dust, lindane is said to have caused irritation of the eyes and respiratory passages in particularly sensitive individuals. However, test applications of a 3% dust mixture with talc on the eyes and nasal mucosa of rabbits produced no 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 lindane using a filter with subsequent recovery with iso-octane and gas chromatographic analysis. An analytical method for lindane 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 lindane or liquids containing lindane where skin contact may occur.
- If employees' clothing may have become contaminated with lindane or liquids containing lindane, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with lindane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of lindane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the lindane, the person performing the operation should be informed of lindane's hazardous properties.
- Where exposure of an employee's body to lindane or liquids containing lindane 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 lindane should be removed promptly and non-impervious clothing which becomes contaminated with liquids containing lindane should be re-

moved immediately and not reworn until the lindane is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where lindane or liquids containing lindane may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquids containing lindane should be immediately washed or showered with soap or mild detergent and water to remove any lindane.

• Skin that becomes contaminated with solid lindane should be promptly washed or showered with soap or mild detergent and water to remove any lindane.

• Eating and smoking should not be permitted in areas where solid lindane is handled, processed, or stored.

• Employees who handle lindane or liquids containing lindane 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 lindane may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of insecticides, scabicides, pediculicides, and vermifuges	Process enclosure; general dilution ventilation; personal protective equipment
Application as a pesticide on plant, animal, household, and agricultural premises and equipment	Personal protective equipment
Manufacture of lindane	Process enclosure; 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 lindane or liquids containing lindane 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 lindane or liquids containing lindane get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If lindane or liquids containing lindane soak 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 lindane, 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 lindane or liquids containing lindane 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 lindane 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 lindane should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Lindane may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

Lindane appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

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 5, 1974.

RESPIRATORY PROTECTION FOR LINDANE

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 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.
500 mg/m³ or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
1000 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 1000 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 lindane; 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 1000 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Lithium Hydride

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: LiH
- Synonyms: None
- Appearance and odor: Off-white, translucent solid which is odorless.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for lithium hydride is 0.025 milligram of lithium hydride per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Lithium hydride 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: Lithium hydride causes sneezing, coughing, and severe irritation of the nose and throat. Lithium hydride can cause severe eye and skin burns. If swallowed, the mouth, trachea, and esophagus may be burned. Inadvertent ingestion of lithium hydride may cause nausea, muscle twitches, mental confusion, blurring of vision, coma, and death.

2. Long-term Exposure: None reported. Nervous system damage has been reported from high short-term exposure.

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 lithium hydride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to lithium hydride 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 lithium hydride exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of lithium hydride might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Lithium hydride is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Eye disease: Lithium hydride is a severe eye irritant and may cause tissue damage. Persons with pre-existing eye conditions 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**

Lithium hydride dust is a severe irritant of the eyes, respiratory tract, and skin due to the formation of lithium hydroxide and its caustic action on moist surfaces. The inherent toxicity of the lithium ion is high; a few milliequivalents in the plasma give rise to signs and symptoms of serious nervous system effects: anorexia, nausea, tremor, muscle twitches, apathy, mental confusion, blurring of vision, coma and death. Exposure of animals to concentrations of 5 to 55 mg/m^3 of lithium hydride caused sneezing and coughing; levels of 10 mg/m^3 corroded the body fur and skin of the legs, and there was occasionally severe inflammation of the eyes and nasal septum. Lesions of the nose and paws were similar to thermal burns and were attributed to the alkalinity of

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 hydrolysis product of lithium hydride. The explosion of a cylinder of lithium hydride led to eye contact and swallowing of a small amount of the dust by a technician. The resulting burns caused scarring of both corneas, with strictures of the larynx, trachea, bronchi and esophagus; delayed death occurred. Exposure of humans to 0.5 mg/m³ caused eye and skin irritation; 0.025 mg/m³ caused sneezing, to which some degree of tolerance was acquired. Although unlikely to occur from industrial exposures, ingestion will cause severe burns of the mouth and esophagus. Restricted sodium intakes are reported to increase the toxicity of lithium.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 7.95
2. Boiling point (760 mm Hg): Decomposes at very high temperatures
3. Specific gravity (water = 1): 0.78
4. Vapor density (air = 1 at boiling point of lithium hydride): Not applicable
5. Melting point: 686 C (1267 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): Reacts to form hydrogen gas and lithium caustic
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Moisture and carbon dioxide, even in concentrations normally in air; heat
2. Incompatibilities: Contact with oxidizers, halogenated hydrocarbons, and acids will cause fires and explosions. Contact with water will cause formation of flammable and explosive hydrogen gas. The heat of the reaction may be sufficient to cause ignition.
3. Hazardous decomposition products: Toxic gases and vapors (such as lithium hydride oxide) may be released in a fire involving lithium hydride.
4. Special precautions: Solid lithium hydride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: 200 C (392 F) (may ignite spontaneously in moist air even at ambient temperatures)
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Smother with nitrogen or other inert gas, or by covering containers, or cover with dry graphite or dry dolomite.

- **Warning properties**

According to Grant, "in rats, rabbits, and guinea pigs, it (lithium hydride dust) has been observed to cause irritation and inflammation in the eyes at concentrations which were very irritating to the respiratory tract." Grant states that even very low concentrations can produce respiratory irritation. According to the AIHA *Hygienic Guide*, "well-fitted respirators of the half mask type, when used with dust filters, protect adequately to 0.1 mg/m³," because "persons with some degree of adaptation complain of eye and nose irritation at concentrations above 0.1 mg/m³ . . . ."

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 lithium hydride 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 lithium hydride or liquids containing lithium hydride.
- 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 lithium hydride at or above an airborne concentration of 0.1 mg/m³.

• If employees' clothing has had any possibility of being contaminated with lithium hydride or liquids containing lithium hydride, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with lithium hydride or liquids containing lithium hydride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of lithium hydride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the lithium hydride, the person performing the operation should be informed of lithium hydride's hazardous properties.

• Where there is any possibility of exposure of an employee's body to lithium hydride, liquids containing lithium or airborne concentrations of lithium hydride exceeding 0.5 mg/m³, 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 lithium hydride should be removed immediately and not reworn until the lithium hydride 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 lithium hydride or liquids containing lithium hydride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to lithium hydride or liquids containing lithium hydride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with lithium hydride should be immediately brushed to remove any solid lithium hydride from the skin and washed or showered with copious quantities of water to remove any lithium hydride.

• Workers subject to skin contact with lithium hydride or liquids containing lithium hydride should wash any areas of the body which may have contacted lithium hydride at the end of each work day.

• Eating and smoking should not be permitted in areas where lithium hydride or liquids containing lithium hydride are handled, processed, or stored.

• Employees who handle lithium hydride or liquids containing lithium hydride 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 lithium hydride may occur and control methods which may be effective in each case:

Operation	Controls
Use in powder metallurgy; use in manufacture of buoyancy devices, fuel cells, and portable field generators; use in manufacture of reducing agent and propellant	General dilution ventilation; process enclosure; local exhaus ventilation; personal protective equipment
Use as a shielding material for thermal neutrons in nuclear industry; use as a desiccant; use as a condensing agent in organic synthesis; use in a condensation polymerization; use in manufacture of electronic tubes and in ceramics	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as an intermediate in manufacture of lithium aluminum hydride and lithium amide	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 lithium hydride or liquids containing lithium hydride 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 lithium hydride or liquids containing lithium hydride get on the skin, immediately flush the contaminated skin with large amounts of water. If lithium hydride or liquids containing lithium hydride 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 lithium hydride, 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 lithium hydride or liquids containing lithium hydride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the

lithium hydride. 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 DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If lithium hydride is spilled, the following steps should be taken:

1. Remove all igntion sources.
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. Avoid contact with water.

• Waste disposal method:

Lithium hydride may be disposed of in dry sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Lithium Hydride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR LITHIUM HYDRIDE

Condition	Minimum Respiratory Protection* Required Above 0.025 mg/m³
Particulate Concentration	
0.1 mg/m³ or less	Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
1.25 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.
25 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
50 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 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.
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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of lithium hydride; 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 50 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for LPG

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_6 – C_3H_8 – C_4H_8 – C_4H_{10} mixture
- Synonyms: Liquefied petroleum gas; bottled gas
- Appearance and odor: Colorless, odorless gas (a foul-smelling odorant is usually added).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for LPG is 1000 parts of LPG per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1800 milligrams of LPG per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

LPG can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to LPG can cause lightheadedness and drowsiness. Greater exposure may also cause unconsciousness and death. Contact with the liquid may also cause frostbite and 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 LPG.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to LPG at potentially hazardous levels.

- **Summary of toxicology**

LPG in gaseous form acts as a simple asphyxiant and a central nervous system depressant. In liquid form it may cause frostbite, as well as skin irritation. Toxicologic data are meager, and no chronic systemic effects have been reported from industrial exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 42– 58 depending on relative amounts of ingredients
2. Boiling point (760 mm Hg): −40 to −0.5 C (−40 to 31 F)
3. Specific gravity (water = 1): 0.5 to 0.58
4. Vapor density (air = 1 at boiling point of LPG): 1.6 to 2.0
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Propane: 8.6 atm.; Butane: 2.1 atm.
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much greater 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 carbon monoxide) may be released in a fire involving LPG.
4. Special precautions: LPG will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: 405 to 450 C (761 to 842 F)
3. Flammable limits in air, % by volume: Lower: 1.9; Upper: 9.5 (estimated)
4. Extinguishant: Stop flow of gas

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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• **Warning properties**

1. Odor Threshold: Propane is the main constituent of LPG, according to the *Documentation of TLV's*. The odor threshold of propane (20,000 ppm) is 20 times the permissible exposure limit (1000 ppm).

2. Eye Irritation Level: Since propane is the main constituent of LPG, and since the eye irritation threshold of propane is above its lower flammable limit, eye irritation does not restrict respirator selection either for propane or for LPG

3. Evaluation of Warning Properties: The odor threshold of propane is 20 times higher than its permissible exposure limit. On the basis of the judgment that propane does not have adequate warning properties, for the purposes of this guideline, LPG is also assumed not 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**

Sampling and analyses may be performed by utilizing a combustible gas meter. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure LPG may be used. An analytical method for LPG 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 the skin from becoming frozen from contact with liquid LPG or from contact with vessels containing liquid LPG.

• Any clothing which becomes wet with liquid LPG should be removed immediately and not reworn until the LPG has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid LPG may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to LPG may occur and control methods which may be effective in each case:

Operation	Controls
Use in chemical industry as feedstock in catalytic cracking in manufacture of petrochemicals and polymers	Process enclosure; general dilution ventilation
Use as an internal combustion engine fuel	General dilution ventilation
Use in manufacture of synthetic rubber	Process enclosure; general dilution ventilation
Use as a fuel for industrial space and wall heating, air conditioning, and water heating	General dilution ventilation
Use as a fuel for drying agricultural products; use as a low sulfur fuel for cutting, soldering, and brazing	General dilution ventilation
Use as a fuel to augment public supply; to increase BTU content of manufactured gas	General dilution ventilation

Use as an aerosol propellant for shaving lather, window cleaners, starch sprays, room deoderants, insecticides, and pharmaceuticals	General dilution ventilation
Use as an agricultural tool in flame cultivation, non-selective cultivation, and weed control	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 liquid LPG gets into the eyes, flush the eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Do not use hot water for eye flushing. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid LPG gets on the skin, immediately flush the contaminated skin with water. If liquid LPG soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of LPG, 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 AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If LPG 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.

• Waste disposal method:

LPG may be disposed of by burning at a safe location or in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "LPG," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Underwriters' Laboratories: *LPG.*

RESPIRATORY PROTECTION FOR LPG

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
19,000 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 19,000 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 Magnesium Oxide 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: MgO
- Synonyms: Magnesia fume
- Appearance: White fume.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for magnesium oxide fume is 15 milligrams of magnesium oxide fume per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for magnesium oxide fume a Threshold Limit Value of 10 mg/m³.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Magnesium oxide fume can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. Short-term Exposure: Magnesium oxide fume may cause irritation of the eyes and nose. It may also cause a metal fume fever. Symptoms of metal fume fever include chills, fever, headache, tightness of chest, cough, weakness, tiredness, dryness of the nose and mouth, muscular pain, nausea, and vomiting.

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 magnesium oxide fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to magnesium oxide 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 magnesium oxide fume exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of magnesium oxide fume 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**

Magnesium oxide fume mildly irritates the eyes and nose. Examination of 95 workers exposed to an unspecified concentration of magnesium oxide dust revealed slight irritation of the eyes and nose; the magnesium level in the serum of 60% of those examined was above the normal upper limit of 3.5 mg%. Experimental subjects exposed to fresh magnesium oxide fume developed metal fume fever, an illness similar to influenza; their symptoms included fever, cough, oppression in the chest, and a leukocytosis. There are no reports of metal fume fever resulting from industrial exposure. Metal magnesium slivers produce a gaseous reaction and cause a slow-healing burn with ulceration, but this has not been reported for magnesium oxide.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 40.3
2. Boiling point (760 mm Hg): 3582 C (6480 F) (solid)
3. Specific gravity (water = 1): Solid = 3.58
4. Vapor density (air = 1 at boiling point of magnesium oxide fume): Not applicable
5. Melting point: 2800 C (5072 F) (solid)

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): 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: Magnesium oxide fume reacts violently with chlorine trifluoride.

3. Hazardous decomposition products: None

4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Magnesium oxide fume may cause mild 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 magnesium oxide fume on a cellulose membrane filter, followed by treatment with nitric acid, and atomic absorption spectrophotometric analysis. An analytical method for magnesium oxide 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.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to magnesium oxide fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fabrication of alloys for aircraft, ships, automobiles, boats, tools, machinery, and military equipment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from casting of metal and alloys	Local exhaust ventilation; general dilution ventilation
Liberation from fabrication of metal	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 magnesium oxide 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 magnesium oxide fume are inadvertently released, ventilate the area of release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Magnesium Oxide Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Magnesium," *Hygienic Guide Series*, Detroit, Michigan, 1960.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

RESPIRATORY PROTECTION FOR MAGNESIUM OXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate Concentration	
150 mg/m³ or less	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.
7,500 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 7,500 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 Health Guideline for Malathion

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: $C_{10}H_{19}O_6PS_2$
- Synonyms: O,O-Dimethyl dithiophosphate of diethyl mercaptosuccinate; O,O-dimethyl S-(1,2-dicarbethoxyethyl) phosphorodithiocite
- Appearance and odor: Colorless to brown liquid with a mild skunk-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for malathion is 15 milligrams of malathion per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended a permissible exposure limit of 15 mg/m^3 averaged over a work shift of up to ten hours per day, forty hours per week. The NIOSH Criteria Document for Malathion should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Malathion can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Malathion is one the least toxic of the organophosphate insecticides. Very large exposures are required to cause symptoms. After inhalation of malathion, 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 the vision, tearing, runny nose, headache, and watering of the mouth. After swallowing malathion, 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 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 heartbeat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to malathion may make a person more susceptible to the effects of this and related chemicals.

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 malathion.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to malathion 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 or recent exposure to anticholinesterase agents would be expected to be at increased risk from exposure. Examination of the respiratory system, liver, and attention to the cholinesterase levels in the blood should be stressed.

—Cholinesterase determination: Malathion can cause depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the erythrocytes should be measured by using medically acceptable biochemical tests before employment (or exposure) in order to establish an individual baseline

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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value, which should be the mean of two ChE activity measurements, taken at least one day apart.

—14" x 17" chest roentgenogram: Malathion causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Malathion is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Liver function tests: Malathion 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, with the exception of the cholinesterase determination which should be performed quarterly or at any time overexposure is suspected or signs and symptoms of toxicity occur.

• **Summary of toxicology**

Malathion is a mild anticholinesterase agent; absorption may occur from inhalation of the mist, from skin absorption of solutions, or from ingestion. Malathion is less toxic to humans than most anticholinesterase agents because it is metabolized in the liver to an inactive form. However, ingestion of 50 to 90 cc of a 50% solution of malathion in a petroleum hydrocarbon base caused severe intoxication; the human LD50 is estimated to be about 1 g/kg. Signs and symptoms of intoxication by anticholinesterase agents are caused by the inactivation of the enzyme cholinesterase, which results in the accumulation of acetylcholine at synapses in the nueromuscular system, and secretory glands. After inhalation of extremely high concentrations, respiratory and ocular effects may appear simultaneously. Respiratory effects include tightness in the chest, wheezing, laryngeal spasms, and excessive salivation. 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. Effects on the central nervous system may include giddiness, confusion, ataxia, and slurred speech. In a group of workers with maximum exposure of 56 mg/m^3 for 5 hours and an average of 3.3 mg/m^3, the cholinesterase levels in the blood were not significantly lowered and no one exhibited signs of cholinesterase inhibition. In a human experiment in which 4 men were exposed 1 hour daily for 42 days to 84.8 mg/m^3, there was moderate irritation of nose and conjunctiva but there were no cholinergic signs or symptoms.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 330
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.23
4. Vapor density (air = 1 at boiling point of malathion): Not applicable
5. Melting point: 2.8 C (37 F)
6. Vapor pressure at 20 C (68 F): 0.00004 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0145
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Starts to decompose at 49 C (140 F) but is not hazardous.
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 in a fire involving malathion.
4. Special precautions: Malathion will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible.

• **Warning properties**

Since malathion has a negligible vapor pressure, warning properties are not considered.

Grant states that "undiluted technical liquid malathion dropped on a rabbits's eye caused slight immediate irritation with conjunctival hyperemia and edema of the lids, but the eye returned to normal in twenty-four hours."

The *Documentation of TLV's* notes that workers exposed to 84.8 mg/m^3 experienced moderate 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**

An analytical method for malathion 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 malathion.
- Non-impervious clothing which becomes contaminated with malathion should be removed promptly and not reworn until the malathion is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid malathion may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to malathion, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with malathion should be promptly washed or showered with soap or mild detergent and water to remove any malathion.
- Employees who handle malathion should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Eating and smoking should not be permitted in areas where malathion is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to malathion may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of pesticide products	Process enclosure; local exhaust ventilation; personal protective equipment
Application as an insecticide for treatment of grain, nut, fruit, and fiber crops; grasses, seeds, and tobacco; animals; agricultural premises	Personal protective equipment
Manufacture of malathion	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 malathion or formulations containing malathion 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 malathion or formulations containing malathion get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If malathion or formulations containing malathion penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of malathion, 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 malathion or formulations containing malathion 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 malathion 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:

Malathion may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR MALATHION

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate or Vapor Concentration	
150 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
750 mg/m³ or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s) and dust, fume, and mist 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, fume, and mist filter(s), 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.
5000 mg/m³ or less	A powered chemical cartridge respirator with a full facepiece, helmet, or hood, an organic vapor cartridge, and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. 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 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 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.

**If an employee informs his employer that he is experiencing eye irritation from malathion while wearing a half- or quarter-mask respirator, the employer should provide an equivalent respirator with a full facepiece, helmet, or hood.

Occupational Health Guideline for Maleic Anhydride

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: $(CHCO)_2O$
- Synonyms: 2,5-Furanedione; cis-butenedioic anhydride; toxilic anhydride
- Appearance and odor: Colorless or white solid with a penetrating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for maleic anhydride is 0.25 part of maleic anhydride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1 milligram of maleic anhydride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Maleic anhydride 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: Maleic anhydride dust and vapor may cause irritation of the eyes, nose, throat, and skin. On contact with the skin, maleic anhydride may not cause an immediate burning sensation, especially if the skin is dry. If the solid form is allowed to remain in contact with moist tissues, burn may occur. Upon inhalation of dust or vapors, a person may experience coughing, sneezing, and burning of the throat. If the dust or vapors get into a person's eyes, irritation, sensitivity to light, and double vision may occur.

2. Long-term Exposure: Repeated or prolonged exposure to maleic anhydride may cause chronic skin or eye irritation. An allergic type of skin rash and asthma may also occur.

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 maleic anhydride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to maleic anhydride 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 maleic anhydride would be expected to be at increased risk from exposure. Examination of the eyes and respiratory tract 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**

Maleic anhydride in the form of a vapor, fume, or dust is a severe irritant of the eyes; it is both an irritant and sensitizer of both the skin and respiratory tract, and may produce asthma on repeated exposures. In a carcinogenesis experiment with a few rats injected subcutaneously with 1 mg maleic anhydride in oil twice weekly for 61 weeks, 2 of 3 surviving animals developed fibrosarcomas which appeared 80 weeks after the start of the experiment. Workers exposed to vapors from heated maleic anhydride developed an intense burning sensation in the eyes and throat, with cough and vomiting; exposure to high fume concentrations caused photophobia, double vision, and a sensation of seeing rings around lights. Exposure of humans to a concentration of

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 to 8 mg/m³ of air resulted in nasal irritation within 1 minute and eye irritation after 15 to 20 minutes. Among workers repeatedly exposed to 5 to 10 mg/m³ there was ulceration of nasal mucous membranes, chronic bronchitis, and some asthma. The dust on dry skin may result in a delayed burning sensation, but on moist skin the sensation is almost immediate, producing erythema which may progress to vesiculation. Prolonged or repeated exposure also may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.1
2. Boiling point (760 mm Hg): 202 C (396 F)
3. Specific gravity (water = 1): 1.43 (solid); 1.3 (melt)
4. Vapor density (air = 1 at boiling point of maleic anhydride): 3.38
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): 0.16 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble but reacts slowly and dissolves
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Maleic anhydride is decomposed by water at temperatures above 66 C (150 F).
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with alkali metals, caustics, and amines may cause polymerization if temperature is greater than 66 C (150 F).
3. Hazardous decomposition products: Toxic gases and vapors (such as irritating fume of unburned material and carbon monoxide) may be released in a fire involving maleic anhydride.
4. Special precautions: None

- **Flammability**

1. Flash point: 102 C (215 F) (closed cup)
2. Autoignition temperature: 477 C (890 F)
3. Flammable limits in air, % by volume: Lower: 3.4 (calculated); Upper: 7.1
4. Extinguishant: Alcohol foam, carbon dioxide. Dry chemical, multi-purpose dry chemical, or loaded stream fire extinguishing media should not be used because of the possibility of an explosion due to the probable reaction of basic compounds in these extinguishing media with maleic anhydride.

- **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, "at a concentration of 2 mg/m³ a faint odor is noticed."
2. Eye Irritation Level: Exposure to a concentration of 6 to 8 mg/m³ maleic anhydride results in eye irritation within 15 to 20 minutes, according to the *Hygienic Guide*, which also states that "a tendency for eye irritation at levels of approximately 1 mg/m³ has been observed."

Grant reports that maleic anhydride is a "crystalline material which powders and sublimes readily, producing fumes which are powerfully irritating to the eyes and respiratory tract." Grant gives no quantitative information, however.

3. Other Information: The *Hygienic Guide* notes that at a concentration of 6 to 8 mg/m³ "persons not accustomed to handling maleic anhydride report definite nasal irritation within 1 minute."
4. Evaluation of Warning Properties: Through its odor maleic anhydride can be detected at a concentration of only twice the TLV. In addition, the *Hygienic Guide* states that eye irritation can occur at the TLV.

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 maleic anhydride 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 solid or liquid maleic anhydride or liquids containing maleic anhydride.

• Clothing contaminated with maleic anhydride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of maleic anhydride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the maleic anhydride, the person performing the operation should be informed of maleic anhydride's hazardous properties.

• Non-impervious clothing which becomes contaminated with maleic anhydride should be removed promptly and not reworn until the maleic anhydride 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 solid or liquid maleic anhydride or liquids containing maleic anhydride contacting the eyes.

• Where there is any possibility of exposure of an employee's body to solid or liquid maleic anhydride or liquids containing maleic anhydride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Where there is any possibility that employees' eyes may be exposed to solid or liquid maleic anhydride or liquids containing maleic anhydride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with maleic anhydride should be promptly washed or showered with soap or mild detergent and water to remove any maleic anhydride.

• Employees who handle solid or liquid maleic anhydride or liquids containing maleic anhydride 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 maleic anhydride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of polyester resins for automobile bodies, structural building panels, molded boats, and chemical storage tanks	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of fumaric acid (as food acidulant) and polyester; use in manufacture of alkyld resins as enamels, interior flat finishes, automotive finishes, printing inks, reactive plasticizers, and marine paints and varnishes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of detergents and lubricating additives as dispersant and wetting agent; use in manufacture of drying oils	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of tall oil resins as general coating and industrial dip cotaing; use in manufacture of terpene resins as shellac substitutes, in aniline inks, as protective coatings on paper, in metal foil, cellulose films, and natural and synthetic fiber	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of chlorendic anhydride for fire-retardant polyester resins, as expoxy hardener, component of military paints, manufacture of extreme pressure lubricants; and use in organic synthesis and in production of chemical intermediates	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 maleic anhydride gets into the eyes, wash eyes immediately with copious amounts of water, lifting the lower and upper lids occasionally. If irritation or other eye problems are present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If maleic anhydride gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If maleic anhydride or liquids containing maleic anhydride 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 maleic anhydride, 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 maleic anhydride 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 maleic anhydride 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.
3. Large quantities should be collected in the most convenient and safe manner for reclamation or disposal in a secured sanitary landfill.

• Waste disposal methods:

Maleic anhydride may be disposed of:

1. By making packages of maleic anhydride in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving maleic anhydride in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By placing maleic anhydride in closed containers and depositing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR MALEIC ANHYDRIDE

Condition	Minimum Respiratory Protection* Required Above 0.25 ppm
Particulate or Vapor Concentration	
12.5 ppm or 50 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 ppm or 1000 mg/m³ or less	A powered air-purifying respirator with an organic vapor cartridge and a high efficiency particulate filter and a full facepiece, helmet, or hood.
500 ppm or 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 500 ppm or 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.
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 Health Guideline for Manganese

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: Mn
- Synonyms: None
- Appearance: Gray solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for manganese is a ceiling level of 5 milligrams of manganese per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Manganese can affect the body if it is inhaled. Manganese can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of fumes with high concentrations of manganese and its oxides may bring about "metal fume fever." Symptoms of metal fume fever are chills and fever, upset stomach, vomiting, dryness of the throat, cough, weakness, and aching of the head and body. Symptoms often occur several hours after exposure to fumes and usually last for only a day.

2. Long-term Exposure: Prolonged or repeated exposure to manganese may affect the nervous system with difficulty in walking and balancing, weakness or cramps in the legs, hoarseness of the voice, trouble with memory and judgment, unstable emotions or unusual irritability. If high exposure continues, a person may have poor coordination, difficulty in speaking clearly, or shaking or tremor of the arms or legs. A person may also have hallucinations or uncontrollable laughter or crying. The respiratory system may be affected by a condition known as "manganese pneumonia," which may result in symptoms and signs of coughing, fever, chills, general aching of the body, chest pain, and other common signs of pneumonia.

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 manganese.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to manganese 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 alcoholism, psychiatric, neurologic, or pulmonary diseases or liver dysfunction would be expected to be at increased risk from exposure. Examination of the respiratory tract, hemopoietic system, and kidneys should be stressed.

—14" x 17" chest roentgenogram: Manganese causes pneumonitis or metal fume fever. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Manganese is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

—A complete blood count: Manganese has been reported to cause blood changes. 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.

—Urinalysis: Since kidney damage has been observed in humans exposed to manganese, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged

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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sediment. Determination of manganese level in urine may be helpful in assessing exposure.

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.

• **Summary of toxicology**

Inhalation of manganese dust or fume primarily affects the central nervous system; high concentrations cause the influenza-like illness termed manganese pneumonitis. Manganese acts either as a direct neurotoxin, or it adversely affects certain neuroenzymes. Manganese fume causes a disease quite similar to Parkinsonism after 6 months to 2 years of exposure. Initially there is headache; asthenia; restless sleep or somnolence; change in personality with psychomotor instability associated with restlessness, irritability, and a tendency to either cry or laugh inappropriately. This is followed by an intermediate phase with visual hallucinations, double vision; impaired hearing; uncontrollable impulses; mental confusion; euphoria; and normal reaction to painful stimuli. In the advanced phase, the subject exhibits possible anemia; excessive salivation; disorders of the basal ganglia of Parkinsonian type, such as mask-like facies, muscle weakness, muscle rigidity, tremor of the uppper extremities and head, and impaired gait. High concentrations of manganese dust produce fever and chills similiar to mental fume fever. During human exposure to manganese fume there is dryness and irritation of the throat, a sweet or metallic taste followed by substernal tightness, constriction in the chest, and a dry cough. Several hours following exposure the subject develops chills, lassitude, malaise, fatigue, frontal headache, low back pain, muscle cramps, and occasionally blurred vision, nausea, and vomiting. Physical examination reveals fever, perspiration, dyspnea, rales throughout the chest, and tachycardia; in some instances there has been a reversible reduction in pulmonary vital capacity. Leukopenia has been reported in 4 out of 16 cases of manganese poisoning, although there is no convincing evidence that any changes in the blood should be regarded as specific or diagnostic of manganism.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 54.94
2. Boiling point (760 mm Hg): 2097 C (3806 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of manganese): Data not available
5. Melting point: 1245 C (2273 F)
6. Vapor pressure at 1227 C (2240 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Not pertinent
8. Evaporation rate (butyl acetate = 1): Not pertinent
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Data not available

• **Warning properties**

Grant states that "local contact of manganese with the cornea does not appear to be a problem industrially."

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of manganese. 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 manganese in a filter, followed by atomic absorption spectrophotometric analysis. An analytical method for manganese 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.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to manganese may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during welding operations	Local exhaust ventilation; respiratory protective devices; dilution ventilation
Liberation during casting of molten ferro-manganese	Local exhaust ventilation
Liberating during bagging of manganese ore	Local exhaust ventilation; respiratory protective devices and dust suppression with water
Liberation during mixing and pressing of dry battery depolarization	Local exhaust ventilation
Liberation during grinding of ore containing manganese	Local exhaust ventilation; respiratory protective devices and dust suppression with water
Liberation during arc burning of manganese-hardened steel in repair and manufacture programs	Local exhaust ventilation; respiratory protective devices; dilution ventilation
Liberation from top of submerged arc electric furnace	General dilution ventilation and process enclosure, if possible
Liberation of dust during ore extraction	General dilution ventilation; respiratory protective devices
Liberation during metal finishing operations of high manganese steel	Local exhaust ventilation; respiratory protective equipment
Liberation of dust during crushing of ferro-manganese metal prior to shipment; during dumping, weighing, and mixing operations in ceramics and glass manufacture for pigmentation and coloration purposes	Local exhaust ventilation; respiratory protective equipment
Liberation from formulation of proprietary mixtures for paint and varnish manufacture	Local exhaust ventilation; respiratory protective equipment
Liberation of dioxide and sulfate during manufacture and application of fertilizers	Local exhaust ventilation
Liberation of dust during manufacture of manganese soap and wood preservatives; manufacture of safety matches, signal flares, fire-works, and strikers; during mixing and kiln operations of brick manufacture	Local exhaust ventilation
Liberation of dusts during manufacture and utilization of oxidation catalysts, such as hopcalite, manganese acetate, and naphthenate	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 manganese, 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 manganese 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 manganese is spilled, the following steps should be taken:

1. Remove all ignition sources.

2. 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:

Manganese may be disposed of:

1. By making packages of manganese in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. By dissolving manganese in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on manganese, look up manganese 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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RESPIRATORY PROTECTION FOR MANGANESE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Dust or Mist Concentration	
25 mg/m³ or less	Any dust and mist respirator, except single-use respirators.
50 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
50 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
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.
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.
10,000 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 10,000 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 Inorganic Mercury

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: Hg
- Synonyms: Quicksilver
- Appearance and odor: Silvery, mobile, odorless *liquid.*

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for mercury is a ceiling level of 0.1 milligram of mercury per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 0.05 mg/m^3 averaged over an eight-hour work shift. The NIOSH Criteria Document for Inorganic Mercury should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Mercury can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhaled mercury vapor may cause headaches, cough, chest pains, chest tightness, and difficulty in breathing. It may also cause chemical pneumanitis. In addition, it may cause soreness of the mouth, loss of teeth, nausea, and diarrhea. Liquid mercury may irritate the skin.

2. Long-term Exposure: Repeated or prolonged exposure to mercury liquid or vapor causes effects which develop gradually. The first effects to occur are often fine shaking of the hands, eyelids, lips, tongue, or jaw. Other effects are allergic skin rash, headache, sores in the mouth, sore and swollen gums, loose teeth, insomnia, excess salivation, personality change, irritability, indecision, loss of memory, and intellectual deterioration.

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 mercury.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to mercury 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 allergies or known sensitization to mercury, chronic respiratory disease, nervous system disorders, or kidney disease would be expected to be at increased risk from exposure. Examination for any signs or symptoms of unacceptable mercury absorption such as weight loss, insomnia, tremors, personality changes, or other evidence of central nervous system involvement, as well as evidence of kidney damage, should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to mercury, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Determination of mercury level in urine may be helpful in assessing extent of absorption.

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
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• **Summary of toxicology**

Acute exposure to mercury at high levels causes severe respiratory irritation, digestive disturbances, and marked renal damage; chronic mercurialism, the form of intoxication most frequently caused by occupational exposure, is characterized by neurologic and psychic disturbances, anorexia, weight loss, and stomatitis. Skin absorption of inorganic mercury probably adds to the toxic effects of vapor inhalation. Intraperitoneal injection of metallic mercury in rats has produced sarcomas. Exposure of humans to mercury vapor in concentrations of 1.2 to 8.5 mg/m^3 causes cough, chest pain and dyspnea, leading to bronchitis and pneumonitis. Metallic mercury readily vaporizes at room temperature, and the vapor has no warning properties. At low levels, the onset of symptoms resulting from chronic exposure is insidious; fine tremors of the hands, eyelids, lips and tongue are often the presenting complaint. Coarse jerky movements and incoordination may interfere with the fine movements considered necessary for writing and eating. Psychic disturbances such as insomnia, irritability, and indecision occur; headache, excessive fatigue, anorexia, digestive disturbances, and weight loss are common; stomatitis with excessive salivation is sometimes severe; muscle weakness has been reported. Proteinuria may occur, but is relatively infrequent. Mercury has been reported to be capable of causing sensitization dermatitis. Examination of urine for mercury may be of value. There is no "critical" level of mercury in urine above or below which poisoning cannot be seen. Various observers have suggested from 0.1 to 0.5 mg of Hg/l of urine as having clinical significance. Mercury, particularly organic forms, is known to adversely affect the fetus if the mother is exposed during pregnancy.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 200.6
2. Boiling point (760 mm Hg): 357 C (674 F)
3. Specific gravity (water = 1): 13.5
4. Vapor density (air = 1 at boiling point of mercury): Not applicable
5. Melting point: −39 C (-38 F)
6. Vapor pressure at 20 C (68 F): 0.0012 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.002
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with acetylene, acetylene products, or ammonia gases may form solid products that are sensitive to shock and which can initiate fires of combustible materials.
3. Hazardous decomposition products: None
4. Special precautions: Mercury can attack copper and copper alloy materials.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: Mercury is odorless.
2. Eye Irritation Level: Grant states that "when mercury metal droplets are in the epithelium, rather than the corneal stroma or anterior chamber, they are extruded rapidly with little reaction, as was reported in a patient who was sprayed forcefully with metallic mercury and was observed to have many fine silvery globules beneath the epithelium of the cornea . . . .

"Mercury metal in contact with the conjunctiva has been shown in rabbits to be absorbed and ultimately to be detectable in the urine. While in contact with the conjunctiva, metallic mercury produced no clinical signs of conjunctivitis, but histologically an inflammatory reaction has been demonstrable. External contact with mercury vapor has repeatedly been observed to induce a characteristic discoloration of the crystalline lens (mercurialentis)." Mercurialentis also is caused by systemic poisoning "from absorption of mercury vapor through the respiratory tract, the skin, and the gastrointestinal tract."

For the purposes of this guideline, mercury is not treated as an eye irritant.

3. Evaluation of Warning Properties: Mercury has no warning properties, according to the *Hygienic Guide.*

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of mercury. 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 mercury with a three-section solid phase sampler, followed by analysis with an atomic absorption spectrophotometer. An analytical method for mercury 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 liquid mercury.
- If employees' clothing may have become contaminated with mercury, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with mercury should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of mercury from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the mercury, the person performing the operation should be informed of mercury's hazardous properties.
- Non-impervious clothing which becomes contaminated with mercury should be removed promptly and not reworn until the mercury is removed from the clothing.

SANITATION

- Workers subject to skin contact with liquid mercury should wash with soap or mild detergent and water any areas of the body which may have contacted mercury at the end of each work day.
- Skin that becomes contaminated with mercury should be promptly washed or showered with soap or mild detergent and water to remove any mercury.
- Eating and smoking should not be permitted in areas where mercury is handled, processed, or stored.
- Employees who handle mercury 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 mercury may occur and control methods which may be effective in each case:

Operation	Controls
Use as a liquid cathode in electrolytic production of chlorine and caustic soda from brine	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use during manufacture and repair of industrial and medical apparatus; use during manufacture of inorganic and organic compounds for use as pesticides, antiseptics, germicides, and skin preparations, and miscellaneous applications as chemical intermediates, preservatives, and pigments	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use in preparation of amalgams for use in tooth restorations, chemical processing, and molding operations; use during manufacture of mildew-proof paints and marine antifouling agents	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of organic mercurials; use in manufacture of batteries, lamps, and power tubes; manufacture of tungsten-molybdenum wire and rods; use in manufacture of inorganic salts for use as catalysts in production of urethanes, vinyl chloride monomers, anthraquinone derivatives, and other miscellaneous chemicals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping

Operation	Controls
Use as a chemical intermediate and in the manufacture of felt; as a flotation agent in manufacture of bowling balls; use as a laboratory reagent or as a working fluid in instruments	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use as a conductor during construction and maintenance of military and nuclear power systems, in mercury-stem boilers, and in air-rectifiers	General dilution ventilation; personal protective equipment; meticulous housekeeping
Liberation during roasting and smelting operations	General dilution ventilation; local exhaust ventilation
Use in manufacture of explosives; in preparation of amalgams for use in artificial jewelry	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use in manufacture of compounds for pulp and paper industry as controls for biological growths	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation during mining and subsequent refining of ore containing cinnabar	General dilution ventilation; personal protective equipment; meticulous housekeeping

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 mercury 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 mercury gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid mercury penetrates 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 mercury, 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 large quantities of mercury have been swallowed or mercury has been swallowed repeatedly 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 PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If mercury is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material for reclamation using commercially available mercury vapor depressants or specialized vacuum cleaners.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Mercury as Hg," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR INORGANIC MERCURY

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate or 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.
28 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 28 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 mercury. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Organo (Alkyl) Mercury

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 organo (alkyl) mercury compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Ethylmercuric chloride

- Formula: C_2H_5HgCl
- Synonyms: Chloroethylmercury; ceresan
- Appearance and odor: Colorless, odorless solid.

Dimethylmercury

- Formula: $(CH_3)_2Hg$
- Synonyms: Mercury dimethyl
- Appearance and odor: Colorless liquid with a weak, sweetish odor.

Diethylmercury

- Formula: $(C_2H_5)_2Hg$
- Synonyms: Mercury diethyl
- Appearance and odor: Colorless liquid with a weak, sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for organo (alkyl) mercury is 0.01 milligram of organo (alkyl) mercury per cubic meter of air (mg/m^3) averaged over an eight-hour work shift, with a ceiling level of 0.04 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Organo (alkyl) mercury 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**

Organo (alkyl) mercury compounds may cause damage to the central nervous system and are irritants of the eyes, respiratory tract, and skin. Symptoms of methyl and ethyl mercury intoxication may occur weeks to months after an acute exposure to toxic concentrations. The symptoms of acute and chronic intoxication from both compounds are similar and include numbness and tingling of the lips, hands and feet, staggering, joint pain, narrowing of vision, hearing difficulties, and emotional disturbances. With severe intoxication the symptoms are usually irreversible. Severe intoxication also results in periods of spasticity and jerking movements of the arms and legs, head or shoulders, and bouts of groaning, moaning, shouting, or crying. Other symptoms are dizziness, increased watering of the mouth, watering of the eyes, nausea, vomiting, and diarrhea or constipation. Infants born to mothers who have been exposed to large amounts of methyl mercury have shown mental retardation and cerebral palsy with convulsions. The symptoms of exposure to methoxyethyl mercury are loss of appetite, diarrhea, weight loss, and fatigue. Kidney damage has occurred. The alkyl mercury halides are irritating to the eyes, upper respiratory tract, and skin and may cause severe skin rash and burns. Allergic skin rashes 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 organo (alkyl) mercury.

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

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Occupational Safety and Health Administration

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to organo (alkyl) mercury 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, the kidneys, and eyes should be stressed. The skin should be examined for evidence of chronic disorders.

—Blood test: Analysis of the blood for mercury may be useful in monitoring absorption.

—Urinalysis: Since kidney damage has been observed in humans exposed to organo mercury, 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**

Organo (alkyl) mercury compounds cause dysfunction of the central nervous system and irritate the eyes, mucous membranes, and and skin. Symptoms of methyl and ethyl mercury intoxication may occur weeks to months after an acute exposure to toxic concentrations. The symptoms of acute and chronic intoxication from both compounds are similar and include numbness and tingling of the lips, hands, and feet; ataxia; dysarthria; concentric constriction of the visual fields (tunnel vision); impairment of hearing; and emotional disturbances. With severe intoxication, the symptoms are usually irreversible. Severe intoxication also results in incontinence, periods of spasticity and jerking movements of the limbs, head or shoulders, and bouts of groaning, moaning, shouting, or crying; less frequent symptoms are dizziness, hypersalivation, lacrimation, nausea, vomiting, and diarrhea or constipation. An epidemic of intoxication from ingestion of fish contaminated with methyl mercury occurred in the Minamata district in Japan, and methyl mercury intoxication is often referred to as Minamata disease. Infants born to mothers with exposure to large amounts of methyl mercury had mental retardation and cerebral palsy with convulsions; methyl mercury has a strong effect on cell division and chromosome segregation, which may produce chromosomal alterations. The biological half-life in humans for methyl mercury is about 70 days; since elimination is slow, irregular, and individualized, there is a considerable risk of an accumulation of mercury to toxic levels. A precise relationship between atmospheric levels and concentrations of mercury in blood or urine cannot be shown. Clinical observations indicate that concentrations of 50 to 100 ug mercury/100 ml of whole blood may be associated with symptoms of intoxication; concentrations around 10 to 20 ug mercury/100 ml are not associated with symptoms. In a study of 20 workers engaged in the manufacture of organic mercurials and exposed for 6 years to mercury concentrations in air between 0.01 and 0.1 mg/m^3, there was no evidence of physical impairment or clinical laboratory abnormalities. The symptoms of exposure to methoxyethyl mercury are anorexia, diarrhea, weight loss, and fatigue, and are probably due to inorganic mercury; kidney damage with albuminuria, and occasionally a nephrotic syndrome, has occurred. The alkyl mercury halides are irritating to the eyes, mucous membranes, and skin and may cause severe dermatitis and burns; skin sensitization has occasionally occurred.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Ethylmercuric chloride**

1. Molecular weight: 265.1
2. Boiling point (760 mm Hg): Sublimes above 40 C (104 F)
3. Specific gravity (water = 1): 3.48
4. Vapor density (air = 1 at boiling point of ethylmercuric chloride): 9.2
5. Melting point: 192 C (378 F)
6. Vapor pressure at 20 C (68 F): Much less than 1
7. Solubility in water, g/100 g water at 20 C (68 F): 0.00014
8. Evaporation rate (butyl acetate = 1): Data not available

• **Physical data—Dimethylmercury**

1. Molecular weight: 230.7
2. Boiling point (760 mm Hg): 95 C (203 F)
3. Specific gravity (water = 1): 3.2
4. Vapor density (air = 1 at boiling point of dimethylmercury): 7.9
5. Melting point: −80 C (−112 F) (approximately)
6. Vapor pressure at 20 C (68 F): 50 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

• **Physical data—Diethylmercury**

1. Molecular weight: 258.7
2. Boiling point (760 mm Hg): 159 C (318 F)
3. Specific gravity (water = 1): 2.5
4. Vapor density (air = 1 at boiling point of diethylmercury): 8.9
5. Melting point: Data not available (very low)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
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: Elevated temperatures cause decomposition to flammable and explosive hydrocarbon gases.
2. Incompatibilities: Contact with strong oxidizers such as chlorine may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases

and vapors (such as toxic mercury fumes and carbon monoxide) may be released in a fire involving organo (alkyl) mercury.

4. Special precautions: Liquid organo (alkyl) mercury will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Ethylmercuric chloride: Not applicable; Dimethylmercury and diethylmercury: Data not available

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: The American National Standards Institute (ANSI) states that many alkyl mercury compounds "are disagreeable in odor."

2. Irritation Levels: ANSI states that "the organomercurials are severe skin, eye, and mucous membrane irritants. The first complaints following surface contact may be delayed for several hours and are usually those of local warmth and redness, which progress to blistering. In cases of repeated exposure, skin sensitization may occur."

3. Evaluation of Warning Properties: Not all alkyl mercury compounds have adequate 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 organo (alkyl) mercury. 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 organo (alkyl) mercury 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 organo (alkyl) mercury or liquids containing organo (alkyl) mercury.

• If employees' clothing has had any possibility of being contaminated with organo (alkyl) mercury or liquids containing organo (alkyl) mercury, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with organo (alkyl) mercury should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of organo (alkyl) mercury from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the organo (alkyl) mercury, the person performing the operation should be informed of organo (alkyl) mercury's hazardous properties.

• Where there is any possibility of exposure of an employee's body to organo (alkyl) mercury or liquids containing organo (alkyl) mercury, 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 organo (alkyl) mercury should be removed immediately and not reworn until the organo (alkyl) mercury 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 organo (alkyl) mercury or liquids

containing organo (alkyl) mercury contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to organo (alkyl) mercury or liquids containing organo (alkyl) mercury, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with organo (alkyl) mercury should be immediately washed or showered with soap or mild detergent and water to remove any organo (alkyl) mercury.

• Workers subject to skin contact with organo (alkyl) mercury or liquids containing organo (alkyl) mercury should wash with soap or mild detergent and water any areas of the body which may have contacted organo (alkyl) mercury at the end of each work day.

• Eating and smoking should not be permitted in areas where organo (alkyl) mercury or liquids containing organo (alkyl) mercury are handled, processed, or stored.

• Employees who handle organo (alkyl) mercury or liquids containing organo (alkyl) mercury 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 organo (alkyl) mercury may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture/ production for use as fungicides and slimicides	Replacement/ substitution; dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during processing mercury ore and during mining and extraction operations	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in treating and disinfecting of seeds and bulbs	Replacement/ substitution; general dilution ventilation; personal protective equipment
Liberation during utilization (spraying) of seeds and bulbs	Replacement/ substitution; general dilution ventilation; personal protective equipment
Use as a wood, timber, and paper preservative and slimicide; liberation during analysis at seed control stations	Replacement/ substitution; 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 organo (alkyl) mercury or solutions containing organo (alkyl) mercury 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 solid organo (alkyl) mercury or solutions containing organo (alkyl) mercury get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solid organo (alkyl) mercury or solutions containing organo (alkyl) mercury penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention.

• **Breathing**

If a person breathes in large amounts of organo (alkyl) mercury, 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 organo (alkyl) mercury 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 organo (alkyl) mercury compounds are 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 solid form, collect for reclamation or disposal in sealed containers in a secured sanitary landfill.
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 reclaimed or collected for reclamation or disposal in sealed containers in a secured sanitary landfill.

• Waste disposal methods:

Organo (alkyl) mercury may be disposed of:

1. If in the solid form, by collecting for reclamation or for disposal in sealed containers in a secured sanitary landfill.
2. 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 reclaimed or collected for reclamation or disposal in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR ORGANO (ALKYL) MERCURY

Condition	Minimum Respiratory Protection* Required Above 0.01 mg/m³
Particulate or Vapor Concentration	
0.5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
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 organo (alkyl) mercury vapors and particulates. 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 organo (alkyl) mercury; 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.

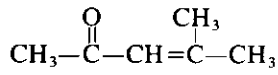
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR MESITYL OXIDE

INTRODUCTION

This guideline summarizes pertinent information about mesityl oxide 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:** Isobutenyl methyl ketone, isopropylidene acetone, methyl isobutenyl ketone, 4-methyl-3-penten-2-one
- **Identifiers:** CAS 141-79-7; RTECS SB4200000; DOT 1229, label required: "Flammable Liquid"
- **Appearance and odor:** Oily, colorless or pale yellow liquid with a strong odor like peppermint

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.16
2. Boiling point (at 760 mmHg): 130°C (266°F)
3. Specific gravity (water = 1): 0.856
4. Vapor density (air = 1 at boiling point of mesityl oxide): 3.4
5. Melting point: -46°C (-50.8°F)
6. Vapor pressure at 20°C (68°F): 8 mmHg; at 25°C (77°F), 9.5 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 3
8. Evaporation rate (butyl acetate = 1): 0.85
9. Saturation concentration in air (approximate): At 20°C (68°F), 1.05% (10,500 ppm); at 25°C (77°F), 1.25% (12,500 ppm)
10. Ionization potential: 9.08 eV

- **Reactivity**

1. Incompatibilities: Contact with oxidizing agents may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving mesityl oxide.
3. Caution: Mesityl oxide may dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 30.6°C (87°F) (closed cup)
2. Autoignition temperature: 344°C (652°F)
3. Flammable limits in air, % by volume: Lower, 1.3; upper, 8.8
4. Extinguishant: Carbon dioxide, dry chemical, or alcohol foam
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: 0.45 ppm
2. Eye irritation level: 25 ppm
3. Evaluation of warning properties for respirator selection: Because of its odor, mesityl oxide 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 mesityl oxide is 25 parts of mesityl oxide per million parts of air (ppm) [100 milligrams of mesityl oxide per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 10 ppm (40 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 15 ppm (60 mg/m^3) as a TWA for a normal 8-hour workday or a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 25 ppm (100 mg/m^3) (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 mesityl oxide

	Exposure limits ppm	mg/m³
OSHA PEL TWA	25	100
NIOSH REL TWA	10	40
ACGIH TLV® TWA	15	60
STEL	25	100

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Mesityl oxide 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 mesityl oxide by mice or rabbits produced narcosis, tissue destruction (necrosis) of the liver, hemorrhage and edema of the lungs, alimentary tract distention, and death. Subchronic inhalation of mesityl oxide by rats, mice, or guinea pigs caused congestion of the liver and lungs and damage to the kidney tubules.

2. *Effects on humans:* Exposure of workers to mesityl oxide has caused centeral nervous system depression and narcosis.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to mesityl oxide can cause headache, dizziness, breathing difficulty (dyspnea), and unconsciousness. Irritation of the eyes, nose, and throat can also occur.

2. *Long-term (chronic):* Exposure to mesityl oxide 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 mesityl oxide, 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 mesityl oxide 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 mesityl oxide. 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.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to mesityl oxide 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 mesityl oxide 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 mesityl oxide may also be used. A detailed sampling and analytical method for mesityl oxide may be found in the *NIOSH Manual of Analytical Methods* (method number 1301).

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 mesityl oxide.

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

SANITATION

Clothing which is contaminated with mesityl oxide 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 mesityl oxide from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of mesityl oxide's hazardous properties.

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

Skin that becomes contaminated with mesityl oxide 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 mesityl oxide 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 mesityl oxide 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 mesityl oxide

Operations	Controls
During spray application of lacquers and stains; during use as a solvent	Process enclosure, local exhaust ventilation, personal protective equipment
During use as a paint and varnish remover and carburetor cleaner	General dilution ventilation, personal protective equipment
During preparation and application of roll-coating inks	Process enclosure, local exhaust ventilation, personal protective equipment
During flotation processes for selective benefaction of ores	Natural 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 mesityl oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

If mesityl oxide 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 mesityl oxide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If mesityl oxide gets on the skin, wash it immediately with soap and water. If mesityl oxide 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 mesityl oxide 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 mesityl oxide, absorb on paper towels and place in 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 mesityl oxide vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing mesityl oxide may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Mesityl oxide should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing mesityl oxide 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 mesityl oxide

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 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 500 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)
	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 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 10 ppm (40 mg/m^3) (TWA).

Occupational Health Guideline for Methoxychlor

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: $C_{16}H_{15}Cl_3O_2$
- Synonyms: 2,2-Bis(p-methoxyphenyl)-1,1,1-trichloroethane
- Appearance and odor: Colorless to tan solid with a slight fruity odor (or emulsifiable solution in heavy aromatic naphtha).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methoxychlor is 15 milligrams of methoxychlor per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for methoxychlor a Threshold Limit Value of 10 mg/m³.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methoxychlor can affect the body if it is inhaled. It can also affect the body if it is swallowed.

- **Effects of overexposure**

There are no reported effects in humans from exposure to methoxychlor. Animal experiments have shown that this chemical may produce trembling, convulsions, and mild kidney and liver damage. Women may be at increased risk.

- **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 methoxychlor.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methoxychlor 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 methoxychlor exposure.

—Liver disease: Methoxychlor 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: Methoxychlor 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.

—Convulsive and other neurologic disorders: Methoxychlor causes convulsions and other neurologic disorders 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**

Methoxychlor affects the nervous system and causes convulsions in animals. The oral LD50 in rats is 6 g/kg; the fatal oral dose in humans is estimated to be 450 g. Although some liver tumors were observed in rats fed up to 2000 ppm in the diet, it is not possible to evaluate adequately the carcinogenicity of methoxychlor due to inadequate reporting of these data; three other feeding studies produced no evidence of carcinogenesis. Dogs fed a daily diet containing 4 g/kg body weight developed signs of chlorinated hydrocarbon intoxication, including fasciculations, tremor, hyperesthesia, tonic seizures, and tetanic convulsions after 5 to 8 weeks; most of the dogs died within 3 weeks after onset of effects. Rabbits given 200 mg/kg orally per day died

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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after 4 to 5 doses; autopsy findings included mild liver damage and nephrosis. In mice given 5 mg orally over 3 days and in rats given 20 mg, there was a uterotrophic effect manifested as a marked increase in weight of the uterus. There are no reported effects in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 345.7
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.41
4. Vapor density (air = 1 at boiling point of methoxychlor): Not applicable
5. Melting point: 78 or 86 C (172 or 187 F) (dimorphic)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 0.01
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 hydrogen chloride and carbon monoxide) may be released when methoxychlor decomposes.
4. Special precautions: Methoxychlor will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: For solids: Dry chemical, water, carbon dioxide, and foam

- **Warning properties**

Since the vapor pressure of this substance is very low, and since methoxychlor decomposes upon heating, warning properties are not considered.

Methoxychlor 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 methoxychlor 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 repeated or prolonged skin contact with methoxychlor or liquids containing methoxychlor.
- Non-impervious clothing which becomes contaminated with methoxychlor should be removed promptly and not reworn until the methoxychlor is removed from the clothing.

SANITATION

- Skin that becomes contaminated with methoxychlor should be promptly washed or showered with soap or mild detergent and water to remove any methoxychlor.
- Employees who handle methoxychlor or liquids containing methoxychlor 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 methoxychlor may occur and control methods which may be effective in each case:

Operation	Controls
Use as an agricultural insecticide on fruits, vegetables, foliage, crops, and ornamentals; agricultural premises; and animal treatment	Personal protective equipment
Liberation during formulation and manufacture for use as an agricultural insecticide	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.

• **Skin Exposure**

If methoxychlor or liquids containing methoxychlor get 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 end of work.

• **Breathing**

If a person breathes in large amounts of methoxychlor, move the exposed person to fresh air at once.

• **Swallowing**

When methoxychlor or liquids containing methoxychlor 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.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If methoxychlor 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 methoxychlor should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Methoxychlor may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR METHOXYCHLOR

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Particulate Concentration	
150 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, mist, and fume filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
750 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust, mist, and fume 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, mist, and fume 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.
7500 mg/m³ or less	A powered chemical cartridge respirator with an organic vapor cartridge and a high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 7500 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 Methyl Acetate

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_3COOCH_3
- Synonyms: Acetic acid methyl ester; methyl acetic ester; methyl ethanoate
- Appearance and odor: Colorless liquid with a fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl acetate is 200 parts of methyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 610 milligrams of methyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methyl acetate may cause irritation of the nose, throat, and eyes. Headache, drowsiness, and unconsciousness are also possible. (Several cases of disturbance of vision have been reported from overexposure to this chemical).

2. Long-term Exposure: Prolonged overexposure 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 methyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl acetate 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 methyl acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Methyl acetate 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 methyl acetate 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 methyl acetate is not known as a kidney toxin in humans, the importance of this organ in the excretion of certain chemicals and their metabolites should be considered before exposing persons with impaired kidney function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The vapor of methyl acetate is mildly irritating to the upper respiratory tract and, in higher concentrations, to the eyes. Upon absorption, methyl acetate may be hydrolyzed with the liberation of methanol. The systemic effects, especially the chronic effects, may therefore be similar to those of methanol, and could include atrophy of the optic nerve. Animals exposed to concentrations of approximately 10,000 ppm showed narcosis leading to death in some. Chronic poisoning of 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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by inhalation resulted in pulmonary edema and changes in liver, kidney, and myocardium. Liquid methyl acetate in the eye causes inflammation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 74
  2. Boiling point (760 mm Hg): 57 C (135 F)
  3. Specific gravity (water = 1): 0.94
  4. Vapor density (air = 1 at boiling point of methyl acetate): 2.8
  5. Melting point: −98 C (−144 F)
  6. Vapor pressure at 20 C (68 F): 173 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 24.5
  8. Evaporation rate (butyl acetate = 1): 11.8
- **Reactivity**
  1. Conditions contributing to instability: Heat
  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 methyl acetate.
  4. Special precautions: None
- **Flammability**
  1. Flash point: −10 C (14 F) (closed cup)
  2. Autoignition temperature: 502 C (935 F)
  3. Flammable limits in air, % by volume: Lower: 3.1; Upper: 16
  4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Summer and May report that the odor threshold of methyl acetate is 200 ppm.
  2. Eye Irritation Level: According to Grant, "the vapor at a concentration of 10,000 ppm in air causes irritation of the eyes, nose, and throat in human beings, also in cats." Sax also reports that "the irritant concentration is about 10,000 ppm."
  3. Evaluation of Warning Properties: Since the odor threshold of methyl acetate is at the TLV, 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 methyl acetate 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 methyl acetate may be used. An analytical method for methyl acetate 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).
935).

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 methyl acetate.
- Clothing wet with liquid methyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl acetate, the person performing the operation should be informed of methyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid methyl acetate should be removed immediately and not reworn until the methyl acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl acetate should be promptly washed or showered to remove any methyl acetate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl acetate may occur and control methods which may be effective in each case:

Operation	Controls
Use during preparation of methyl acetone, including methylacetate, methanol, and acetone for use as solvents	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for nitrocellulose and cellulose acetate	General dilution ventilation; personal protective equipment
Liberation during use as a chemical intermediate	General dilution ventilation
Use during spraying of lacquers, paint thinners, and vinyl resin coatings; use of paint removers	Local exhaust ventilation; personal protective equipment
Liberation during preparation of paint removers and lacquer solvents	Local exhaust ventilation; general dilution ventilation
Liberation during preparation of methylacetate or recovery as a by-product from wood carbonization	Local exhaust ventilation
Use during preparation of artificial leather	Local exhaust ventilation; personal protective equipment
Liberation during formulation of lacquers, paints, perfumes, and any vinyl resin coatings	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 methyl acetate 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 methyl acetate gets on the skin, promptly flush the contaminated skin with water. If methyl acetate soaks 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 methyl acetate, 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 methyl acetate 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 methyl acetate 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. Methyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Methyl acetate 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.

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RESPIRATORY PROTECTION FOR METHYL ACETATE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
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. A powered air-purifying chemical cartridge respirator with an organic vapor cartridge. 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 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 10,000 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 Methyl Acetylene

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_4
- Synonyms: Propyne; allylene
- Appearance and odor: Colorless gas with a sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl acetylene is 1000 parts of methyl acetylene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1650 milligrams of methyl acetylene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl acetylene can affect the body if it is inhaled.

- **Effects of overexposure**

Overexposure to methyl acetylene may cause the overexposed person to become drowsy and unconscious.

- **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 methyl acetylene.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to methyl acetylene at potentially hazardous levels.

- **Summary of toxicology**

Methyl acetylene primarily affects the central nervous system. The gas has anesthetic properties at concentrations as high as 42,000 ppm, which is below the LC50 value. At 28,700 ppm for 6 hours daily, 5 days a week for 6 months, most animals survived; there was hyperexcitability, ataxia, tremors, and occasional convulsions, all of which subsided rapidly when the 6-hour exposure period ended. Animals that died or were killed on termination of the study showed pulmonary irritation. Neither acute nor chronic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 40.1
2. Boiling point (760 mm Hg): −23 C (−10 F)
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of methyl acetylene): 1.4
5. Melting point: −103 C (-153 F)
6. Vapor pressure at 20 C (68 F): 3800 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Almost insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable (gas)

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents and chlorine may cause fires and explosions. Methyl acetylene forms compounds with copper and copper alloys that are very sensitive to shock.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl acetylene.
4. Special precautions: Copper or copper alloys containing more than 67% copper should not be used in equipment handling methyl acetylene.

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 11.7

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. Extinguishant: Stop flow of gas

• **Warning properties**

1. Odor Threshold: No quantitative information is available.

2. Eye Irritation Level: Methyl acetylene is not known to be an eye irritant.

3. Evaluation of Warning Properties: Since no quantitative information is available relating its warning properties to air concentrations, 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 methyl acetylene 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 the skin from becoming frozen from contact with liquid methyl acetylene or from contact with vessels containing methyl acetylene.

• Any clothing which becomes wet with liquid methyl acetylene should be removed immediately and not reworn until the methyl acetylene has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl acetylene may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl acetylene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during synthesis of pharmaceuticals and aromatics	General dilution ventilation
Liberation during high-temperature, gas-welding operations using MAPP fuel; liberation from decomposition of magnesium carbide by hydrolysis	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.

• **Breathing**

If a person breathes in large amounts of methyl acetylene, 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 AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If methyl acetylene is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak to disperse gas.
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, keep people

away, and repair the leak or allow the cylinder to empty.

• Waste disposal methods:

Methyl acetylene may be disposed of

1. If in small quantities, by allowing gas to escape into open air at a place where there are no ignition sources.
2. If in larger quantities, by allowing the gas to burn under the supervision of qualified personnel.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Methyl Acetylene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Horn, H. J., Weir, R. J., and Reese, W. H.: "Inhalation Toxicology of Methylacetylene," *A.M.A. Archives of Industrial Health*, 15:20-25, 1957.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR METHYL ACETYLENE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
11,000 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 11,000 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 Methyl Acetylene-Propadiene Mixture

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_4 isomers
- Synonyms: MAPP gas; methyl acetylene-allene mixture; propyne-allene mixture
- Appearance and odor: Colorless gas with a strong, characteristic, foul odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl acetylene-propadiene mixture is 1000 parts of methyl acetylene-propadiene mixture per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1800 milligrams of methyl acetylene-propadiene mixture per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl acetylene-propadiene mixture can affect the body if it is inhaled or if the liquid comes in contact with the skin or eyes

- **Effects of overexposure**

Overexposure to methyl acetylene-propadiene mixture may cause a person to become drowsy or unconscious. Spilled on the skin or in the eyes, it may also cause frostbite.

- **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 methyl acetylene-propadiene mixture.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to methyl acetylene-propadiene mixture at potentially hazardous levels.

- **Summary of toxicology**

Methyl acetylene-propadiene mixture (MAPP) is a gas with anesthetic properties at high concentrations. Animals exposed for 7 hours daily for 16 weeks to 1000 ppm showed no adverse effects; at 5000 ppm there was only slight decline in body and organ weights of some rats, but no pathological changes. In another study of the main component of the mixture, methyl acetylene, rats survived a single 6-hour exposure at 42,000 ppm, which resulted in anesthesia with rapid recovery; autopsy of the rats 9 days after exposure showed bronchiolitis and pneumonitis. Some human subjects indicated that they could detect 25 ppm, and most could detect 100 ppm. The musty odor was considered to be strong at 1000 ppm and quite objectionable at higher concentrations. No adverse effects have been reported from repeated exposures. The liquefied gas may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 40
2. Boiling point (760 mm Hg): −37.8 to −20 C (−36 F to −4 F)
3. Specific gravity (water = 1): 0.576 (liquid)
4. Vapor density (air = 1 at boiling point of methyl acetylene-propadiene mixture): 1.48
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Not pertinent
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with

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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copper alloys containing more than 6% copper may form explosive copper compounds.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl acetylene-propadiene mixture.

4. Special precautions: Methyl acetylene-propadiene mixture will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: 454 C (850 F)
3. Flammable limits in air, % by volume: Lower: 3.4; Upper: 10.8
4. Extinguishant: Stop flow of gas

• **Warning properties**

1. Odor Threshold: According to the Biochemical Research Laboratory of the Dow Chemical Company, MAPP has a strong odor which is easily detectable at 100 ppm.
2. Eye Irritation Level: MAPP is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of MAPP is below the permissible exposure limit, MAPP 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 methyl acetylene-propadiene mixture 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 frozen from contact with liquid methyl acetylene-propadiene mixture or from contact with vessels containing liquid methyl acetylene-propadiene mixture.

• Any clothing which becomes wet with liquid methyl acetylene-propadiene mixture should be removed immediately and not reworn until the methyl acetylene-propadiene mixture has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl acetylene-propadiene mixture may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl acetylene-propadiene mixture may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from flame hardening, metallizing, brazing, welding and cutting	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 methyl acetylene-propadiene mixture gets into the eyes, flush eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Do not use hot water for eye flushing. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid methyl acetylene-propadiene mixture gets on the skin, immediately flush the contaminated skin with water. If liquid methyl acetylene-propadiene mixture soaks through the clothing, remove the clothing immediately and flush the skin with water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of methyl acetylene-propadiene mixture, 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 AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If methyl acetylene-propadiene mixture 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.

• Waste disposal method:

Methyl acetylene-propadiene mixture may be disposed of by burning at a safe location or in a suitable combustion chamber.

• Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Methylene Acetylene-Propadiene Mixture," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Dow Chemical Company, Biochemical Research Laboratory: *Material Safety Data Sheet – Methyl Acetylene-Propadiene Mixture*, Midland, Michigan, 1964.

• Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.

• Torkelson, T. R., and Rowe, V. K.: "Results of Repeated Inhalation by Laboratory Animals and a Limited Human Sensory Study of a Mixture of Saturated and Unsaturated C_3 and C_4 Hydrocarbons (MAPP Industrial Gas)," *American Industrial Hygiene Association Journal*, 25:554-559, 1964.

• Underwriters' Laboratories: *Methyl Acetylene-Propadiene Mixture.*

RESPIRATORY PROTECTION FOR METHYL ACETYLENE-PROPADIENE MIXTURE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
5000 ppm or less	A gas mask with a chin-style canister providing protection against methyl acetylene-propadiene mixture.
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
20,000 ppm or less	A gas mask with a front- or back-mounted canister providing protection against methyl acetylene-propadiene mixture. 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 20,000 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 methyl acetylene-propadiene mixture. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Methyl Acrylate

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: $CH_2=CHCOOCH_3$
- Synonyms: Methyl propenoate
- Appearance and odor: Clear, colorless liquid with a sharp, sweet, and fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl acrylate is 10 parts of methyl acrylate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of methyl acrylate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl acrylate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methyl acrylate may cause irritation of the eyes, nose, throat, and lungs. Death may be caused by lung damage from breathing high air levels or from swallowing it.

2. Long-term Exposure: Prolonged contact with the skin or eyes may result in severe damage.

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 methyl acrylate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl acrylate 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 methyl acrylate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl acrylate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Methyl acrylate is absorbed through the skin. It also is a defatting agent and can cause drying and cracking. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methyl acrylate 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 methyl acrylate is not known as a kidney toxin in humans, the importance of this organ in the excretion of certain chemicals and their metabolites should be considered before exposing persons with impaired kidney function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The vapor of methyl acrylate is irritating to the conjunctiva and upper respiratory tract. In moderate concentrations there are characteristic lacrimatory effects in man. Animals exposed to high concentrations show marked irritation of the eyes and of the respiratory tract, leading to pulmonary edema. The lowest concentration of vapor producing no significant effect in rodents is 30 ppm. Prolonged contact with the eye or the skin in animals causes severe damage. Skin sensitiza-

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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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tion probably occurs, and fatal doses of the liquid are absorbed through the skin of animals exposed for 24 hours. There are no reports of injury to man from long-term exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 86
  2. Boiling point (760 mm Hg): 80 C (176 F)
  3. Specific gravity (water = 1): 0.96
  4. Vapor density (air = 1 at boiling point of methyl acrylate): 2.95
  5. Melting point: −75 C (−103 F)
  6. Vapor pressure at 20 C (68 F): 68.2 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 5.5
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat and/or lack of appropriate inhibitor concentration can cause methyl acrylate to polymerize violently and burst container.
  2. Incompatibilities: Contact with nitrates and other oxidizing materials, including peroxides and other initiators of polymerization, strong alkalies, and atmospheric moisture may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl acrylate.
  4. Special precautions: Inhibitors do not function in absence of air, so inert gas blankets should not be used.
- **Flammability**
  1. Flash point: −7.8 C (18 F) (closed cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: 2.8; Upper: 25
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: The Manufacturing Chemists Association states that most persons can detect the odor of methyl acrylate at 20 ppm. "Odor detection has little practical value in chronic repeated exposures, since most workers become less sensitive to the odor and will tolerate atmospheric concentrations greater than the threshold limits."
  2. Eye Irritation Level: The MCA states that "irritation of the eyes and mucous membranes is experienced beginning at about 75 ppm."
  3. Evaluation of Warning Properties: Methyl acrylate has 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 methyl acrylate 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 methyl acrylate may be used. An analytical method for methyl acrylate 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 methyl acrylate.
- Clothing wet with liquid methyl acrylate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl acrylate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl acrylate, the person performing the operation should be informed of methyl acrylate's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid methyl acrylate, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Any clothing which becomes wet with liquid methyl acrylate should be removed immediately and not reworn until the methyl acrylate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl acrylate may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methyl acrylate should be immediately washed or showered to remove any methyl acrylate.

• Employees who handle liquid methyl acrylate should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl acrylate may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of thermoplastic coatings; use in manufacture of acrylic fibers; use in synthesis of higher acrylates; during preparation of adhesives and sealants based on methyl acrylate	Local exhaust ventilation; personal protective equipment
Use during polymerization in aqueous emulsions to produce resins for surface coatings and adhesives; use during polymerization in solutions to produce resins for surface coatings and adhesives	Local exhaust ventilation; personal protective equipment
Use during preparation of amphoteric surfactants for use in hair shampoos	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 methyl acrylate 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 methyl acrylate gets on the skin, immediately flush the contaminated skin with water. If methyl acrylate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of methyl acrylate, 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. Properly trained individuals may assist the affected person by administering 100% oxygen.

• **Swallowing**

When methyl acrylate 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 methyl acrylate 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. Methyl acrylate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Methyl acrylate may be disposed of:
1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill in an area where the odor will not be objectionable.
2. By atomizing in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Methyl Acrylate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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• Suvorov, A. P.: "Results of Examinations Carried Out on Workers Exposed to Methyl Acrylate," *Gigiena Truda I Professional Nye Zabolenvanioa*, 15:10, pp. 49-50, October 1971.

RESPIRATORY PROTECTION FOR METHYL ACRYLATE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
75 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 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 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 with a full facepiece 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 Methylal

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: $CH_3OCH_2OCH_3$
- Synonyms: Dimethoxymethane; methyl formal; formal; dimethylacetal formaldehyde
- Appearance and odor: Colorless liquid with a pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylal is 1000 parts of methylal per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3100 milligrams of methylal per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylal 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 methylal may cause irritation of the eyes, nose, and throat, lightheadedness, incoordination, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure to methylal 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 methylal.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylal 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 methylal exposure.

—Skin disease: Methylal 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 methylal 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 methylal 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 methylal 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**

Methylal vapor is a mild respiratory irritant with anesthetic properties. Mice exposed at 11,000 ppm showed mild irritation of the eyes and respiratory tract, as well as incoordination; recovery was rapid after single exposures. At 14,000 ppm, mice showed more respiratory irritation, occasional pulmonary edema, and a greater degree of anesthesia. At the LC50 level of approximately 18,000 ppm, animals died of bronchopneumonia with fatty changes in the liver, kidney, and heart. At 4000 ppm rats were unaffected by daily 6-hour exposures.

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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Skin irritation may be expected due to defatting action by the solvent, and eye irritation if splashing occurs. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 76
  2. Boiling point (760 mm Hg): 44 C (111 F)
  3. Specific gravity (water = 1): 0.86
  4. Vapor density (air = 1 at boiling point of methylal): 2.6
  5. Melting point: −105 C (−157 F)
  6. Vapor pressure at 20 C (68 F): 330 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 33
  8. Evaporation rate (butyl acetate = 1): 23.1
- **Reactivity**
  1. Conditions contributing to instability: Heat, presence of acids
  2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde, and methyl alcohol) may be released in a fire involving methylal.
  4. Special precautions: Methylal will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −18 C (−4 F) (closed cup)
  2. Autoignition temperature: 237 C (459 F)
  3. Flammable limits in air, % by volume: Lower: 1.6; Upper: 17.6
  4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: No quantitative information is available concerning the odor threshold, but Browning notes that it has a slightly pungent odor.
  2. Eye Irritation Level: Grant states that "exposures of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially were found to cause . . . occasional irritation of the eyes but no histologically demonstrable abnormality of the optic nerve or retina."

Patty reports that mice which had received 15 7-hour exposures at 11,000 ppm experienced only mild irritation.

No quantitative information is available, however, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Since there is no useful quantitative information relating warning properties to air concentrations of methylal, 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 methylal vapors using an adsorption tube with subsequent desorption with hexane and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylal may be used. An analytical method for methylal 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 methylal.
- Clothing wet with liquid methylal should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylal from the clothing. If the clothing is to be laundered or

otherwise cleaned to remove the methylal, the person performing the operation should be informed of methylal's hazardous properties.

- Any clothing which becomes wet with liquid methylal should be removed immediately and not reworn until the methylal is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylal may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methylal should be promptly washed or showered to remove any methylal.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylal may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent for adhesives, resins, gums, waxes, and protective coatings; use as a solvent for extraction of alkaloids, barbituates, organic acids, and hydroxy-acids	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of artificial resins; use as a gasoline and diesel fuel additive; use as a special fuel for rocket and jet engines	General dilution ventilation; process enclosure; personal protective equipment
Use as a reaction solvent with acetylene or in Grignard and Reppe reaction; use as a source of formaldehyde and methanol	General dilution ventilation; process enclosure; personal protective equipment
Use as a methylating agent or chemical intermediate	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of perfume	General dilution ventilation; 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 methylal 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 methylal gets on the skin, promptly wash the contaminated skin with water, if the methylal has not already evaporated. If methylal soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methylal, 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 methylal 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 methylal 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, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Methylal should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:
Methylal may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Methylal," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR METHYLAL

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
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 Methyl Alcohol

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_3OH
- Synonyms: Methanol; wood alcohol; Columbian spirits; carbinol
- Appearance and odor: Colorless liquid with a characteristic, pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl alcohol is 200 parts of methyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 260 milligrams of methyl alcohol per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 200 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 800 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Methyl Alcohol should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl alcohol 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: Swallowing methyl alcohol or breathing very high concentrations of methyl alcohol may produce headache, weakness, drowsiness, lightheadedness, nausea, vomiting, drunkenness, and irritation of the eyes, blurred vision, blindness, and death. A person may get better and then worse again up to 30 hours later.

2. Long-term Exposure: Prolonged exposure to higher concentrations of methyl alcohol may result in headaches, burning of the eyes, dizziness, sleep problems, digestive disturbances, and failure of vision. Repeated or prolonged 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 methyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl alcohol 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, and eyes should be stressed.

—Skin disease: Methyl alcohol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be susceptible to the effects of this agent.

—Liver function tests: Methyl alcohol may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Although methyl alcohol has not been proven to be kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Eye disease: Because methyl alcohol may cause optic atrophy and blindness, those with pre-existing eye diseases may be at increased risk from exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. In addition, anyone developing the above-listed conditions or who has been splashed in the eyes 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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has ingested, or otherwise has been exposed to methyl alcohol should be placed under medical surveillance.

• **Summary of toxicology**

Ingestion of methyl alcohol is a well-known cause of optic neuropathy and may be lethal. Severe acidosis may result from ingestion or high exposures. Animals exposed to vapor concentrations above 8000 to 10,000 ppm show narcotic effects progressing from lethargy, to ataxia, to prostration and death in a state of profound acidosis due in part to the metabolic formation of formaldehyde and formic acid. Occupational exposure to high concentrations of methyl alcohol vapor has been reported to cause death or blindness, usually from working in a confined space. A woman died after exposure for 12 hours to vapor concentrations calculated at 4000 to 13,000 ppm. Chronic poisoning manifested by marked diminution of vision and enlargement of the liver has been reported in a workman exposed at levels of 1200 to 8000 ppm for a period of 4 years. Direct skin contact with methy alcohol may cause dermatitis, erythema, and scaling.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 32
2. Boiling point (760 mm Hg): 64.5 C (148 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of methyl alcohol): 1.1
5. Melting point: −98 C (-144 F)
6. Vapor pressure at 20 C (68 F): 97 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): 5.9

• **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 and formaldehyde) may be released in a fire involving methyl alcohol.
4. Special precautions: Methyl alcohol will attack some forms of plastics, rubber, and coatings. It may also react with metallic aluminum at high temperatures.

• **Flammability**

1. Flash point: 11 C (52 F) (closed cup)
2. Autoignition temperature: 385 C (725 F)
3. Flammable limits in air, % by volume: Lower: 6.7; Upper: 36
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: May and Summer report that the odor threshold of methyl alcohol (methanol) is 5900 ppm. The AIHA *Hygienic Guide* states that the odor is faint at 2000 ppm.
2. Eye Irritation Level: The *Hygienic Guide* states that irritation occurs only at high concentrations. Grant states that "external contact of methanol with the eye has been alleged to have caused corneal opacities, but this must be far from the rule .... By exposure of cats to methanol vapors an attempt has been made to induce vacuoles in the corneal epithelium similar to those produced by other solvents, but this has been unsuccessful."

Browning reports that concentrations ranging from 7500 ppm to 69,000 ppm irritate mucous membranes.

3. Evaluation of Warning Properties: Methyl alcohol (methanol) has 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 methyl alcohol. 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 methyl alcohol in an adsorption tube containing silica gel, followed by desorption with water, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl alcohol may be used. An analytical method for methyl alcohol 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 methyl alcohol.
- Clothing wet with liquid methyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl alcohol, the person performing the operation should be informed of methyl alcohol's hazardous properties.
- Any clothing which becomes wet with liquid methyl alcohol should be removed immediately and not reworn until the methyl alcohol is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl alcohol may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl alcohol should be promptly washed or showered to remove any methyl alcohol.
- Eating and smoking should not be permitted in areas where liquid methyl alcohol is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl alcohol may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during application of surface coatings such as shellac, wood dyes, nitrocellulose lacquers, water-proofing formulations, and phenolic resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for rotogravure inks, aniline dyes, and duplicator fluids	General dilution ventilation
Liberation during manual application of methanol as a cleaner for coated surfaces, leather, gloves, and metal and resins surfaces prior to further treatment	General dilution ventilation; personal protective equipment
Liberation during manufacture of formaldehyde by oxidation or dehydrogenation	Local exhaust ventilation; general dilution ventilation
Use in plastics industry to produce plasticizers, softening agents, and acrylic resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use as an intermediate in the preparation of methacrylates, methyl chlorides, methyl ethers, dimethyl sulfate, methyl formate, and methyl bromide	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during application as an extractant in industrial chemical processes such as refinery gasoline and oils and purifying pharmaceuticals such as steroids and hormones	Local exhaust ventilation; general dilution ventilation
Use as a solvent in rubber industry	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 methyl alcohol 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 methyl alcohol gets on the skin, promptly flush the contaminated skin with water. If methyl alcohol soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of methyl alcohol, 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 methyl alcohol 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 methyl 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, 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. Methyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Methyl alcohol 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: "Methyl Alcohol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR METHYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
2000 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.
25,000 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 25,000 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 Methylamine

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_3NH_2
- Synonyms: Monomethylamine; anhydrous methylamine
- Appearance and odor: Colorless gas with an odor like ammonia, but more fishy, particularly at lower concentrations. It can be stored under pressure as a liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylamine is 10 parts of methylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 12 milligrams of methylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylamine 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**

1. Short-term Exposure: Methylamine may cause irritation of the eyes, nose, throat, and lungs. It may also cause coughing and sneezing. Both the liquid and vapor of methylamine are highly irritating to the eyes. Eye injury may occur if proper care is not given immediately. Methylamine solutions may burn the skin.

2. Long-term Exposure: Repeated or prolonged exposure to methylamine may cause irritation of the skin or eyes.

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 methylamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylamine 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 methylamine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylamine might cause exacerbation of symptoms due to its irritant properties.

—Eye disease: Methylamine causes eye damage in animals and eye irritation in humans. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Skin disease: Methylamine in solution 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**

Methylamine gas is a severe eye and respiratory irritant. The LD50 was 0.1 to 0.2 g/kg in rats exposed orally to a 40% aqueous solution of methylamine. One case of bronchitis in a chemical worker has been reported; concentrations measured in the workroom ranged from 2 to 60 ppm; the duration of the exposure was not given. Brief exposures to 20 to 100 ppm are said to produce transient irritation of the eyes, nose, and throat. No symptoms of irritation are produced from longer exposures at less than 10 ppm. One drop of 5% aqueous solution caused conjunctival hemorrhage, superficial corneal opacities, and edema in experimental animals; a

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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40% solution caused corneal damage in rabbits. A 40% solution caused necrosis when applied to the skin of a rabbit. Dermatitis and conjunctivitis are occasionally observed in workers after prolonged exposure to the vapor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 31.1
2. Boiling point (760 mm Hg): −6.32 C (20.6 F)
3. Specific gravity (water = 1): 0.656
4. Vapor density (air = 1 at boiling point of methylamine): 1.1
5. Melting point: −93.5 C (-136.3 F)
6. Vapor pressure at 20 C (68 F): Not pertinent
7. Solubility in water, g/100 g water at 25 C (77 F): 959 cc/100 ml
8. Evaporation rate (butyl acetate = 1): Greater than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of gas or liquid methylamine with mercury or with strong oxidizers will 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 methylamine.
4. Special precautions: Liquid methylamine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable (gas)
2. Autoignition temperature: 430 C (806 F)
3. Flammable limits in air, % by volume: Lower: 5; Upper: 21
4. Extinguishant: Stop flow of gas; use carbon dioxide, alcohol foam, or dry chemical for water solutions

- **Warning properties**

1. Odor Threshold: May reports an odor threshold of 3.3 ppm. Patty reports that "olfactory fatigue occurs readily" upon exposure to methylamine.
2. Eye Irritation Level: Grant reports that methylamine is an eye irritant, but the concentrations producing irritation are not given. Patty, however, reports that "brief exposures to 20 to 100 ppm produce transient eye . . . irritation."
3. Other Information: Patty reports that transitory nose and throat irritation is caused by short exposures to 20 to 100 ppm.
4. Evaluation of Warning Properties: Although the odor threshold of methylamine (3.3 ppm) is well below the permissible exposure limit, methylamine is treated as a material with poor warning properties, since "olfactory fatigue occurs readily." In addition, the irritant effects produced by brief exposures to methylamine are not considered to give adequate warning, since these effects are only transient.

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 methylamine 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 the skin from becoming contaminated with liquid methylamine or solutions containing methylamine or from becoming frozen from contact with vessels containing methylamine.
- Clothing wet with liquid methylamine or solutions containing methylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylamine, the person performing the operation should be informed of methylamine's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid methylamine or solutions

containing methylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Any clothing which becomes wet with methylamine or non-impervious clothing which becomes contaminated with methylamine should be removed immediately and not reworn until the methylamine 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 methylamine or solutions containing methylamine contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid methylamine or solutions containing methylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with methylamine should be immediately washed or showered to remove any methylamine.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylamine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chemical intermediate in production of insecticides, herbicides, and fungicides; use as a chemical intermediate in production of surfactants	Local exhaust ventilation; general dilution ventilation
Use in production of rocket fuels and explosives	Local exhaust ventilation; general dilution ventilation
Use in production of pharmaceuticals and photographic chemicals; intermediate for dyes, textiles, dye assists, rubber, and anti-corrosive chemicals	Local exhaust ventilation; general dilution ventilation
Use as a polymerization inhibitor of hydrocarbons during distillization; use to prevent coagulation and webbing in natural and synthetic latex; use to prevent polymerization in paint removers	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 methylamine or solutions containing methylamine 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 methylamine or solutions containing methylamine get on the skin, immediately flush the contaminated skin with water. If liquid methylamine or solutions containing methylamine 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 methylamine, 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 a solution of methylamine has 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 leaks until cleanup has been completed.

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

1. Remove all ignition sources.
2. Ventilate area of leak to disperse gas.
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, allow to vaporize.

• Waste disposal method:

Methylamine may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR METHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
100 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 100 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 methylamine. Any escape self-contained breathing apparatus with a full facepiece.

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

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR METHYL (n-AMYL) KETONE

INTRODUCTION

This guideline summarizes pertinent information about methyl (n-amyl) ketone 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:** $C_7H_{14}O$
- **Structure:**

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-CH_3$$

- **Synonyms:** n-Amyl methyl ketone, 2-heptanone
- **Identifiers:** CAS 110-43-0; RTECS MJ5075000; DOT 1110
- **Appearance and odor:** Clear, colorless liquid with a penetrating, fruity odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 114.21
2. Boiling point (at 760 mmHg): 151°C (304°F)
3. Specific gravity (water = 1): 0.82
4. Vapor density [air = 1 at boiling point of methyl (n-amyl) ketone]: 3.93
5. Melting point: -35°C (-31°F)
6. Vapor pressure at 20°C (68°F): 2 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.43
8. Evaporation rate (butyl acetate = 1): 0.4
9. Saturation concentration in air (approximate) at 20°C (68°F): 0.27% (2,700 ppm)
10. Ionization potential: 9.33 eV

- **Reactivity**

1. Incompatibilities: Contact with strong acids, alkalies, and oxidizing agents may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving methyl (n-amyl) ketone.
3. Caution: Methyl (n-amyl) ketone will dissolve some forms of plastics, resins, and rubber.

- **Flammability**

1. Flash point: 39°C (102°F) (closed cup)
2. Autoignition temperature: 393°C (740°F)
3. Flammable limits in air, % by volume: Lower, 1.1; upper, 7.9
4. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
5. Class II Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)

- **Warning properties**

1. Odor threshold: 0.35 ppm
2. Evaluation of warning properties for respirator selection: Because of its odor, methyl (n-amyl) ketone 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 methyl (n-amyl) ketone is 100 parts of methyl (n-amyl) ketone per million parts of air (ppm) [465 milligrams of methyl (n-amyl) ketone per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 100 ppm (465 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 (235 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek.

Table 1.—Occupational exposure limits for methyl (n-amyl) ketone

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	100	465
NIOSH REL TWA	100	465
ACGIH TLV® TWA	50	235

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HEALTH HAZARD INFORMATION

• **Routes of exposure**
Methyl (n-amyl) ketone may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• **Summary of toxicology**
Effects on animals: Acute inhalation of methyl (n-amyl) ketone by guinea pigs caused irritation of the mucous membranes, narcosis, and death.

• **Signs and symptoms of exposure**
1. *Short-term exposure (acute):* Exposure to methyl (n-amyl) ketone can cause headaches, dizziness, and irritation of the eyes, nose, and throat.
2. *Long-term exposure (chronic):* Exposure to methyl (n-amyl) ketone 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 methyl (n-amyl) ketone, 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 methyl (n-amyl) ketone 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 methyl (n-amyl) ketone. 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 methyl (n-amyl) ketone 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 methyl (n-amyl) ketone 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 methyl (n-amyl) ketone may also be used if available. A detailed sampling and analytical method for methyl (n-amyl) ketone may be found in the *NIOSH Manual of Analytical Methods* (method number 1301).

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 methyl (n-amyl) ketone.

Workers should be provided with and required to use splash-proof safety goggles where methyl (n-amyl) ketone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with methyl (n-amyl) ketone 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 methyl (n-amyl) ketone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of methyl (n-amyl) ketone's hazardous properties.

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

Skin that becomes contaminated with methyl (n-amyl) ketone 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 methyl (n-amyl) ketone 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 methyl (n-amyl) ketone 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 methyl (n-amyl) ketone, an eye-wash fountain should be provided within the immediate work area for emergency use.

Table 2.—Operations and methods of control for methyl (n-amyl) ketone

Operations	Controls
During use in the spray application of lacquers	Local exhaust ventilation, personal protective equipment
During use in the preparation of synthetic resins, especially for metal roll-coating	Process enclosure, local exhaust ventilation
During use as a solvent for rubber and nitrocellulose	Local exhaust ventilation, personal protective equipment

If methyl (n-amyl) ketone 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 methyl (n-amyl) ketone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If methyl (n-amyl) ketone gets on the skin, wash it immediately with soap and water. If methyl (n-amyl) ketone 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 methyl (n-amyl) ketone 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 methyl (n-amyl) ketone, 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 methyl (n-amyl) ketone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing methyl (n-amyl) ketone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Methyl (n-amyl) ketone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

5. Liquids containing methyl (n-amyl) ketone 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 methyl (n-amyl) ketone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) (substance reported to cause eye irritation or damage—may require eye protection)
	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 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 2,500 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 4,000 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 4,000 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 100 ppm (465 mg/m³) (TWA).

Occupational Health Guideline for Methyl Bromide

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_3Br
- Synonyms: Bromomethane
- Appearance and odor: Colorless liquid or or gas with a chloroform-like odor at high concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl bromide is a ceiling of 20 parts of methyl bromide per million parts of air (ppm). This may also be expressed as 80 milligrams of methyl bromide per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for methyl bromide from 15 ppm to 5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl bromide 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.

- **Effects of overexposure**

1. Short-term Exposure: Methyl bromide may cause headache, dizziness, nausea, vomiting, blurred vision, slurred speech, and convulsions. High concentrations may cause unconsciousness and death. High concentrations may also cause lung irritation resulting in congestion with coughing, chest pain, and shortness of breath. Lung effects may be delayed in onset. Exposure may also result in kidney damage. The liquid splashed on clothing, gloves, or shoes may be held in close contact with the skin and result in skin burns. Blisters commonly appear after several hours. If the exposure is less severe, an itching skin rash may appear after several days. Contact of liquid methyl bromide with the eyes may cause serious injury.

2. Long-term Exposure: Prolonged or repeated exposure to methyl bromide may cause a variety of symptoms and signs mostly due to injury of the central nervous system. These include visual disturbances, slurred speech, numbness of the arms and legs, confusion, shaking, and unconsciousness. The symptoms may stop within a few days after the termination of exposure or may last for several months. Usually recovery is complete.

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 methyl bromide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl bromide 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 careful history and examination of the nervous and respiratory systems should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Methyl bromide may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Methyl bromide is reported to cause pulmonary impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual

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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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basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

• **Summary of toxicology**

Methyl bromide gas is a severe pulmonary irritant and neurotoxin. It is also a narcotic at high concentrations. Rats did not survive when exposed to 12,850 ppm for 6 minutes, but did survive following exposure to 260 ppm for 8 hours; the no-effect level on repeated exposure was 16 ppm for all species. There are numerous reports of human intoxication from accidental exposure associated with its use in fire extinguishers and as a fumigant. Estimates of concentrations which have caused human fatalities range from 8000 ppm for a few hours to 60,000 ppm for a brief exposure. The onset of toxic symptoms is usually delayed, and the latent period may be from 30 minutes to several days. Early symptoms include headache, visual disturbances, nausea, vomiting, and malaise. In some cases eye irritation, vertigo, and tremors of the hands have occurred; the tremors may progress to twitchings and finally to convulsions. The onset of dyspnea may herald the development of pulmonary edema. Tubular damage in the kidneys has been observed in fatal cases. Some who recovered from severe intoxication have had persistent central nervous system effects including vertigo, depression, hallucinations, anxiety, and inability to concentrate. The determination of bromide in human blood has been proposed for the purpose of estimating the severity of exposure; in a few cases, levels of 40 mg/100 ml of blood have been associated with gross disability, while levels of 10 mg/100 ml and less have been followed by complete recovery. The procedure has not been sufficiently verified to recommend it for routine monitoring of occupational exposure. Local contact with the eye by the gas or liquid results in transient irritation and conjunctivitis. Repeated splashes of the liquid on the skin cause marked irritation with vesiculation; less severe exposures result in a dry, scaling, itching dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 94.9
2. Boiling point (760 mm Hg): 3.6 C (38.4 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of methyl bromide): 3.3
5. Melting point: −94 C (−137 F)
6. Vapor pressure at 20 C (68 F): 1.83 atm.
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.1
8. Evaporation rate (butyl acetate = 1): Greater than 1

• **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with aluminum or strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide and carbon monoxide) may be released in a fire involving methyl bromide.
4. Special precautions: Liquid methyl bromide will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: None in standard test method
2. Autoignition temperature: 537 C (999 F)
3. Flammable limits in air, % by volume: (Only in presence of high energy ignition source) Lower: 13.5; Upper: 14.5
4. Extinguishant: Stop flow of gas.

• **Warning properties**

1. Odor Threshold: Both Patty and the AIHA *Hygienic Guide* report that methyl bromide has practically no odor. Grant notes, however, that at extremely high concentrations, methyl bromide has a "sweetish, not unpleasant odor."
2. Eye Irritation Level: Grant reports that methyl bromide "causes no immediate irritation of the eyes, . . . even at severely poisonous concentrations." Following a period of several hours after exposure to the gas, however, the victim may "have lacrimation from irritation of the eyes." Grant states that "local contact of methyl bromide with the eye, either as concentrated vapor or as a splash of liquid, has resulted in no more than transient irritation and conjunctivitis in the few cases in which this accident has been observed." He also reports that exposing a rabbit's eye to pure methyl bromide gas for 1-1/2 minutes resulted in an "immediate loss of surface luster, followed in several hours by a loss of corneal epithelium and much edema of the conjunctivae and lids." The cornea became opaque but began clearing within 5 days. Grant notes that this exposure was far more severe than that which would happen by accident.
3. Other Information: Grant reports that methyl bromide causes no immediate irritation of the "nose or respiratory tract, even at severely poisonous concentrations."
4. Evaluation of Warning Properties: Since methyl bromide has virtually no odor and no immediately irritating effects, it has poor 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 methyl bromide. 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 methyl bromide may be used. An analytical method for methyl bromide is in the *NIOSH* obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, under the title "NIOSH Analytical 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 any possibility of skin contact with liquid methyl bromide.

• Clothing contaminated with liquid methyl bromide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl bromide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl bromide, the person performing the operation should be informed of methyl bromide's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid methyl bromide, 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 liquid methyl bromide should be removed immediately and not reworn until the methyl bromide is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl bromide may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methyl bromide should be immediately washed or showered with soap or mild detergent and water to remove any methyl bromide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl bromide may occur and control methods which may be effective in each case:

Operation	Controls
Use as a space and soil fumigant in agriculture and industry	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in food sterilization for pest control in fruits, vegetables, dairy products, nuts, and grains	General dilution ventilation; local exhaust ventilation
Use in organic synthesis as methylating agent, for preparation of quarternary ammonium compounds and organo-tin derivatives; use as selective solvent in aniline dyes; laboratory procedures	General dilution ventilation; 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 methyl bromide 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 methyl bromide gets on the skin, immediately flush the contaminated skin with water. If methyl bromide soaks 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 methyl bromide, 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 methyl bromide 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 methyl bromide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or 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:

Methyl bromide 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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RESPIRATORY PROTECTION FOR METHYL BROMIDE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Gas Concentration	
200 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.
2000 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or 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 Health Guideline for Methyl Cellosolve

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: $CH_3OCH_2CH_2OH$
- Synonyms: 2-Methoxyethanol; glycol monomethyl ether; ethylene glycol monomethyl ether; methyl oxitol; Ektasolve; Jeffersol EM
- Appearance and odor: Colorless liquid with a mild, non-residual odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl cellosolve is 25 parts of methyl cellosolve per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 80 milligrams of methyl cellosolve per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl cellosolve 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**

1. Short-term Exposure: Overexposure to methyl cellosolve may cause irritation of the eyes, nose, and throat, drowsiness, weakness, and shaking. Swallowing methyl cellosolve may be fatal.

2. Long-term Exposure: Prolonged or repeated exposure may cause headache, drowsiness, weakness, fatigue, staggering, personality change, and decreased mental ability. Anemia and other blood changes may result.

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 methyl cellosolve.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl cellosolve 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 should be stressed.

—A complete blood count: This compound has been shown to affect the hematopoietic system. 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.

—Urinalysis: This compound has caused acute kidney damage in animals and in humans after oral ingestion.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Methyl cellosolve exerts its effects primarily on the hematopoietic and central nervous systems, although the vapor is also a mild irritant. Cases of toxic encephalopathy and macrocytic anemia have been reported from industrial exposures that may have been as low as 25 to 75 ppm. Symptoms were headache, drowsiness, lethargy, and weakness. Manifestations of central nervous system instability included ataxia, dysarthria, tremor, and somnolence. These effects are usually reversible. In acute exposures the central nervous system effects were the more pronounced, while prolonged exposure to lower concentrations produced primarily evidence of depression of erythrocyte formation. Anemia may be pronounced. When exposure was re-

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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duced to 20 ppm, no further cases occurred. The LC50 for 7-hour exposures of rats was 1480 ppm; death was due to lung and kidney injury. Rabbits exposed to 800 ppm and 1600 ppm for 4 to 10 days showed irritation of the upper respiratory tract and lungs, severe glomerulonephritis, hematuria, and albuminuria. Instilled in rabbit eyes, it caused immediate pain, conjunctival irritation, and slight corneal cloudiness which cleared in 24 hours.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 76.1
  2. Boiling point (760 mm Hg): 124 C (256 F)
  3. Specific gravity (water = 1): 1.0
  4. Vapor density (air = 1 at boiling point of methyl cellosolve): 2.6
  5. Melting point: −85 C (−121 F)
  6. Vapor pressure at 20 C (68 F): 6 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): Approximately 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with strong caustics may cause decomposition.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving methyl cellosolve.
  4. Special precautions: Methyl cellosolve will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 42 C (107 F) (closed cup)
  2. Autoignition temperature: 285 C (545 F)
  3. Flammable limits in air, % by volume: Lower: 2.5; Upper: 19.8
  4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: May reports an odor threshold for methyl cellosolve of 60 ppm.
  2. Eye Irritation Level: Grant states that methyl cellosolve, "tested by applying three drops to rabbit eyes, . . . was found to be only slightly irritating, causing only temporary, slight reddening of the conjunctiva." Browning states that the "vapor of methyl cellosolve is irritant to mucous membranes," but does not give concentrations producing this irritation.
  3. Evaluation of Warning Properties: Although the odor threshold of methyl cellosolve is within three times the permissible exposure limit, odor is not considered an adequate warning property. Browning reports that cases of toxic encephalopathy and macrocytic anemia have been reported among workers exposed to concentrations as low as 25 to 75 ppm methyl cellosolve. The latter was present in a solvent mixture including ethanol and cellulose acetate, however.

The AIHA *Hygienic Guide* states that "warning properties, both odor and irritation, are not sufficient to prevent exposure to concentrations which are physiologically significant."

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 methyl cellosolve vapors using an adsorption tube with subsequent desorption with methanol in methylene chloride and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl cellosolve may be used. An analytical method for methyl cellosolve 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 methyl cellosolve.

- Clothing contaminated with liquid methyl cellosolve should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl cellosolve from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl cellosolve, the person performing the operation should be informed of methyl cellosolve's hazardous properties.
- Where exposure of an employee's body to liquid methyl cellosolve 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 liquid methyl cellosolve and any clothing which becomes wet with liquid methyl cellosolve should be removed immediately and such clothing should not be reworn until the methyl cellosolve is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl cellosolve may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid methyl cellosolve should be immediately washed or showered to remove any methyl cellosolve.
- Employees who handle liquid methyl cellosolve should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl cellosolve may occur and control methods which may be effective in each case:

Operation	Controls
Use during spray application or other method involving heat of surface coatings containing solvent, including wood- and wire-coating lacquers, metal coatings, alkyd baking enamels, phenolic varnishes, and epoxy resin coatings	Local exhaust ventilation; personal protective equipment
Use in printing on plastic materials, rotogravure printing, and cellulose acetate pigment printing on textiles	General dilution ventilation; personal protective equipment
Use during non-heat related application of surface coatings containing solvent, including varnishes and lacquers	Local exhaust ventilation; personal protective equipment
Use in manufacture of surface coatings and dyeing agents for stains, lacquers, dyes, and inks	Process enclosure; local exhaust ventilation
Liberation during sealing of moisture-proof cellophane wrappers and packaging	Process enclosure
Liberation during dyeing operations, including cellulose acetate fibers and fabric, rayon, leather dyeing, and wood staining	Process enclosure; general dilution ventilation
Use as an anti-icing agent in JP-4 military jet fuel and as an anti-stall additive in gasoline	General dilution ventilation
Liberation during synthesis of plasticizer and other compounds	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 methyl cellosolve 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 methyl cellosolve gets on the skin, promptly wash the contaminated skin with water. If methyl cellosolve soaks 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 methyl cellosolve, 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 methyl cellosolve 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 methyl cellosolve 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. Methyl cellosolve should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Methyl cellosolve may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR METHYL CELLOSOLVE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
250 ppm or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
1250 ppm or less	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.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Methyl Cellosolve Acetate

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: $CH_3COOCH_2CH_2OCH_3$
- Synonyms: 2-Methoxyethyl acetate; glycol monomethyl ether acetate; ethylene glycol monomethyl ether acetate
- Appearance and odor: Colorless liquid with a mild, ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl cellosolve acetate is 25 parts of methyl cellosolve acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 120 milligrams of methyl cellosolve acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl cellosolve acetate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

Swallowing a large single dose of methyl cellosolve acetate might be fatal. Swallowing repeated smaller doses of methyl cellosolve acetate or repeated breathing of high air levels of methyl cellosolve acetate might cause lung or kidney damage, brain damage, and death. It is unlikely that air levels of methyl cellosolve acetate will be dangerous unless the liquid is heated. Methyl cellosolve acetate might cause eye irritation if splashed in the eyes. Methyl cellosolve acetate can be absorbed through intact skin. If a large amount is absorbed, death may result.

- **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 methyl cellosolve acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl cellosolve acetate 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 methyl cellosolve acetate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl cellosolve acetate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Methyl cellosolve acetate is absorbed through the skin. It also is a defatting agent and may cause dryness and cracking. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Since methyl cellosolve acetate may cause kidney damage 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 methyl cellosolve acetate 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**

Methyl cellosolve acetate is irritating to the upper respiratory tract and is only slightly narcotic. Guinea

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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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pigs and cats exposed to nearly saturated vapor died after some delay; concentrations of 1500 ppm for 7 hours killed cats, while 7000 ppm for 4 hours was lethal to some rats. On repeated exposures, 500 ppm for 8 hours killed some cats. There was irritation of upper respiratory tract, disturbance of equilibrium, drowsiness, and apathy followed by death. These animals had damage to the lung and kidney. There was only slight irritation of the eyes. There was no irritation upon skin contact, but absorption did occur. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 118
  2. Boiling point (760 mm Hg): 145 C (293 F)
  3. Specific gravity (water = 1): 1.01
  4. Vapor density (air = 1 at boiling point of methyl cellosolve acetate): 4.1
  5. Melting point: −65 C (−85 F)
  6. Vapor pressure at 20 C (68 F): 2 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Completely miscible
  8. Evaporation rate (butyl acetate = 1): 0.3
- **Reactivity**
  1. Conditions contributing to instability: Heat
  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 methyl cellosolve acetate.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 44 C (111 F) (closed cup)
  2. Autoignition temperature: 393 C (740 F)
  3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.2
  4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: According to the *Handbook of Organic Industrial Solvents*, the odor threshold of methyl cellosolve acetate is twice the permissible exposure level.
  2. Eye Irritation Level: According to Browning, methyl cellosolve acetate is only slightly irritating to the eyes and mucous membranes. No quantitative information is available concerning what concentrations produce the irritation, however. Union Carbide reports that "five drops of undiluted chemical produced minor injury in rabbit eyes."
  3. Evaluation of Warning Propertes: Since the odor threshold of methyl cellosolve acetate is only twice the permissible exposure level, 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 methyl cellosolve acetate 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 methyl cellosolve acetate may be used. An analytical method for methyl cellosolve acetate 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 methyl cellosolve acetate.
- Clothing wet with liquid methyl cellosolve acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the

removal of methyl cellosolve acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl cellosolve acetate, the person performing the operation should be informed of methyl cellosolve acetate's hazardous properties.

• Non-impervious clothing which becomes contaminated with liquid methyl cellosolve acetate should be removed promptly and not reworn until the methyl cellosolve acetate is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl cellosolve acetate may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid methyl cellosolve acetate should be promptly washed or showered to remove any methyl cellosolve acetate.

• Employees who handle liquid methyl cellosolve acetate 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 methyl cellosolve acetate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent during spray or heat applications of surface coatings, including varnishes, dopes, lacquers, metal lacquers, cellulose lacquers for paper coatings, textile printing, and leather finishes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent during spray or heat applications of adhesives, including polyvinyl formal, polyvinyl butyral, and polyvinyl acetate adhesives	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of photographic film	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during dry cleaning operations	Local exhaust ventilation; personal protective equipment
Use as a solvent during manufacture of surface coatings, including lacquers, dopes, varnishes, nail polishes; use during manufacture of adhesives	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 methyl cellosolve acetate 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 methyl cellosolve acetate gets on the skin, promptly flush the contaminated skin with water. If methyl cellosolve acetate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of methyl cellosolve acetate, 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 methyl cellosolve acetate 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 methyl cellosolve acetate 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. Liquid methyl cellosolve acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Methyl cellosolve acetate 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: "Methyl Cellosolve Acetate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR METHYL CELLOSOLVE ACETATE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
250 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). 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.
4500 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 4500 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 Methyl Chloride

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_3Cl
- Synonyms: Chloromethane
- Appearance and odor: Colorless gas with a faint, sweet odor that is not noticeable at dangerous concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl chloride is 100 parts of methyl chloride per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 200 ppm and a maximum acceptable peak of 300 ppm for 5 minutes in any three-hour period. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for methyl chloride from 100 ppm to 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl chloride 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: Deaths have occurred following single severe or repeated prolonged moderate overexposure. Overexposure may cause dizziness, vomiting, abdominal pain, diarrhea, breathing difficulties, and unconsciousness. Convulsions and disturbances of vision may occur. It may also damage the kidneys, liver, or blood. The symptoms of methyl chloride overexposure are usually delayed in onset. Frostbite may occur from contact with liquefied methyl chloride.

2. Long-term Exposure: Repeated moderate or mild overexposure may cause delayed (24 to 48 hours) onset of dizziness, headache, mental confusion, slurred speech, double vision, and sleepiness. Recovery from the effects of exposure to this chemical may be slow.

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 methyl chloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl chloride 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, liver, and kidneys should be stressed.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Methyl chloride vapor is a narcotic and may cause a toxic encephalopathy. The LC50 for mice for 7-hour exposure was approximately 3000 ppm. At this concentration some species showed pulmonary edema with hemorrhage, moderate centrolobular necrosis of the liver, and tubular damage in the kidney. At 500 ppm repeated daily for 6 hours, there was response in some species, while 300 ppm daily for 64 weeks produced no detectable effects. Human fatalities have occurred from a single severe exposure or less severe prolonged exposures. Severe but nonfatal poisoning in man is characterized by a latent period of several hours, followed by dizziness, nausea, vomiting, double vision, weakness, paralysis, convulsions, and coma; renal or hepatic

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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damage and anemia also occur. Some workers exposed daily to concentrations averaging 195 to 475 ppm showed delayed signs, including weakness, drowsiness, staggering gait, slurred speech, lapses of memory, and cyanosis. The onset is often insidious and may be confused with mild viral illness; more severe intoxication has been mistaken for viral encephalitis or heavy-metal poisoning. Effects may last for a long period following exposure. No effects were seen in other workers exposed to 15 to 195 ppm. Frostbite may result from contact with the liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 50.5
2. Boiling point (760 mm Hg): −24.2 C (−11.6 F)
3. Specific gravity (water = 1): 0.92 (liquid)
4. Vapor density (air = 1 at boiling point of methyl chloride): 1.8
5. Melting point: −97.6 C (−144 F)
6. Vapor pressure at 20 C (68 F): 4.8 atm.
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: Heat, especially when in contact with water or metals such as aluminum, magnesium, and zinc.
2. Incompatibilities: Contact with chemically active metals such as potassium, powdered aluminum, magnesium, and zinc will 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 methyl chloride.
4. Special precautions: Methyl chloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not pertinent (gas)
2. Autoignition temperature: 632 C (1170 F)
3. Flammable limits in air, % by volume: Lower: 7.6; Upper: 19
4. Extinguishant: Stop flow of gas.

- **Warning properties**

May reports an odor threshold of 10 ppm. However, Patty states that methyl chloride has no odor or other warning properties, and Jacobs states that methyl chloride does not have adequate warning properties at higher concentrations.

Methyl chloride is not an eye irritant, according to Grant, even in concentrations which are "dangerously toxic."

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 methyl chloride. 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 methyl chloride. Each measurement should consist of a 5-minute sample or a series of consecutive samples totalling 5 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 methyl chloride on activated carbon, followed by desorption with methanol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl chloride may be used. An analytical method for methyl chloride 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 wet with liquid methyl chloride or from becoming frozen from contact with vessels containing methyl chloride.

• Any clothing which becomes wet with liquid methyl chloride should be removed immediately and not reworn until the methyl chloride has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl chloride may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of silicone resins, and tetramethyl lead; use as a methylating and chlorinating agent; use as a dewaxing agent in petroleum refining; use as a catalyst solvent in production of butyl rubber	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of a variety of other compounds; as an extractant for greases, oils, and resins	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use as a foaming agent in production of plastics; in the manufacture and application of pesticides, pharmaceuticals, and perfumes; as a propellant in aerosols; and use as a refrigerant	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 liquefied methyl chloride gets into the eyes, wash eyes immediately with large amounts of water. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquefied methyl chloride gets on the skin, immediately flush the contaminated skin using soap or mild detergent and water if the methyl chloride has not already evaporated. If liquefied methyl chloride soaks through the clothing, remove the clothing immediately and flush the skin using soap or mild detergent and water. Do not use hot water for skin flushing. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of methyl chloride, 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 AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If methyl chloride is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas.

• Waste disposal method:

Methyl chloride may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR METHYL CHLORIDE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
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 escape self-contained breathing apparatus.

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

Occupational Health Guideline for Methyl 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: CH_3CCl_3
- Synonyms: 1,1,1-trichloroethane; 1,1,1-trichloroethane, stabilized
- Appearance and odor: Colorless liquid with a mild odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl chloroform is 350 parts of methyl chloroform per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1910 milligrams of methyl chloroform per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to a ceiling of 350 ppm (1910 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for 1,1,1-Trichloroethane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl 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: Exposure to methyl chloroform vapor may cause headache, dizziness, drowsiness, unconsciousness, irregular heart beat, and death. Methyl chloroform liquid splashed in the eyes may cause irritation.

2. Long-term Exposure: Prolonged or repeated skin contact with liquid methyl chloroform may cause irritation of the skin. Reproductive abnormalities have been noted in studies of animals exposed to high concentrations of methyl chloroform.

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 methyl chloroform.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, and cardiovascular system should be stressed. The physician should be made aware of any adverse reproductive effects in workers exposed to methyl chloroform.

—Skin disease: Methyl chloroform can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: At high concentrations, methyl chloroform causes liver changes in animals, which justifies consideration of the possible consequences before exposing persons with impaired liver function.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrhythmias, the inhalation of methyl chloroform might cause exacerbation of disorders of the conduction mechanism due to its sensitizing effects on the myocardium.

—Medical warning: Workers should be provided with information advising them of studies in which congenital abnormalities were found following exposure of animals to high concentrations of methyl chloro-

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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form. The physician should be made aware of any reproductive abnormalities in workers.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Methyl chloroform vapor is a narcotic. Repeated exposure of animals to concentrations of 1000 to 10,000 ppm caused liver and lung changes in some species. In dogs, cardiac sensitization to epinephrine occurred at concentrations of 5000 to 10,000 ppm. A number of human fatalities related to industrial exposure in closed spaces have been reported. A 5-minute exposure to 5000 ppm can be expected to produce marked incoordination and anesthesia. Prolonged exposure at this concentration may cause coma and death. Exposure to concentrations in excess of 1000 ppm for 15 minutes, or 2000 ppm for 5 minutes, can be expected to produce a disturbance of equilibrium in the majority of adults. Above 1700 ppm, minor disturbances of equilibrium have been observed, with complaints of headache and lassitude. In controlled human exposures to 500 ppm no effects other than slight, transient eye irritation were noted; at 1000 ppm and above, mild eye irritation was experienced by all subjects, and some became dizzy. Following exposure, most of the compound is eliminated unchanged via the lungs within 48 hours. When placed into the rabbit eye, the liquid caused conjunctival irritation but no corneal damage. Dermatitis may result from repeated skin contact with the liquid.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 133.4
2. Boiling point (760 mm Hg): 74 C (165 F)
3. Specific gravity (water = 1): 1.33
4. Vapor density (air = 1 at boiling point of methyl chloroform): 4.55
5. Melting point: −38 C (−36 F)
6. Vapor pressure at 20 C (68 F): 100 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.07
8. Evaporation rate (butyl acetate = 1): 12.8

• **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong caustics, strong oxidizers, and chemically active metals such as aluminum and magnesium powders, or sodium and potassium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving methyl chloroform.
4. Special precautions: Liquid methyl chloroform will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: None in normal test method.
2. Autoignition temperature: 500 C (932 F)
3. Flammable limits in air, % by volume: (At elevated temperature and pressure) Lower: 7; Upper: 16
4. Extinguishant: Foam, dry chemical, carbon dioxide

• **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that the odor threshold of methyl chloroform may range from 20 to 100 ppm. Both May and Summer give 400 ppm as the odor threshold, however.
2. Eye Irritation Level: The *Hygienic Guide* states that "in controlled human exposures to 500 ppm no effects other than slight, transient eye irritation were noted, but at 1000 ppm and above, mild eye irritation was experienced by all subjects."
3. Evaluation of Warning Properties: Since the odor threshold of methyl chloroform is near or below the permissible exposure limit, and since eye irritation occurs at a concentration only twice the permissible exposure limit, methyl chloroform is treated as a material with adequate 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 methyl 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 methyl chloroform may be used. An analytical method for methyl 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 repeated or prolonged skin contact with liquid methyl chloroform.

• Non-impervious clothing which becomes wet with liquid methyl chloroform should be removed promptly and not reworn until the methyl chloroform is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl chloroform may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methyl chloroform should be promptly washed or showered to remove any methyl chloroform.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl chloroform may occur and control methods which may be effective in each case:

Operation	Controls
Use as solvent in cold cleaning of metals, and plastics; in vapor degreasing; in ultrasonic cleaning; in dyeing and cleaning of fabrics and yarns	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis in polymer manufacture; as primary and carrier solvent in spot cleaners, adhesives, shoe polishes, stain repellants, hair sprays, Mace, insecticides, resins, inks, lubricants, protective coatings, asphalt extraction, and waste water treatment; use in aerosol manufacture as pressure depressant	Process enclosure; local exhaust ventilation
Use as coolant and lubricant in cutting oils on metals; use during printed circuit boards production; liquid Drano production and photographic film processing	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 methyl chloroform 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 methyl chloroform gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If methyl 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 methyl 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 methyl 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, 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 methyl 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.

• Waste disposal method:

Methyl chloroform may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR METHYL CHLOROFORM

Condition	Minimum Respiratory Protection* Required Above 350 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). 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 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 Health Guideline for Methylcyclohexane

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: $CH_3C_6H_{11}$
- Synonyms: Cyclohexylmethane; hexahydrotoluene
- Appearance and odor: Colorless liquid with a faint, benzene-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylcyclohexane is 500 parts of methylcyclohexane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2000 milligrams of methylcyclohexane per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for methylcyclohexane a Threshold Limit Value of 400 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylcyclohexane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methylcyclohexane may cause light-headedness and drowsiness. It may also cause a slight irritation of the eyes, nose, and throat. At high concentrations, it may cause unconsciousness and death.

2. Long-term Exposure: Prolonged exposure to the liquid 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 methylcyclohexane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylcyclohexane 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 methylcyclohexane exposure.

—Skin disease: Methylcyclohexane is a skin 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 methylcyclohexane 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 methylcyclohexane 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 methylcyclohexane 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**

Methylcyclohexane vapor is a mild narcotic. Concentrations of 10,000 to 12,500 ppm were fatal to mice. Rabbits exposed to 3330 ppm for 300 hours showed minor evidence of liver and kidney injury, while 1200 ppm was innocuous for rabbits, and prolonged exposure at 370 ppm was harmless to monkeys. No toxic effects from industrial exposure have been reported. Prolonged

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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or repeated skin contact may produce drying and irritation due to defatting action.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 98
  2. Boiling point (760 mm Hg): 101 C (214 F)
  3. Specific gravity (water = 1): 0.77
  4. Vapor density (air = 1 at boiling point of methylcyclohexane): 3.4
  5. Melting point: −126 C (−196 F)
  6. Vapor pressure at 20 C (68 F): 37 mm Hg
  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
  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 methylcyclohexane.
  4. Special precautions: Methylcyclohexane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −3.9 C (25 F) (closed cup)
  2. Autoignition temperature: 250 C (482 F)
  3. Flammable limits in air, % by volume: Lower: 1.2; Upper: 6.7
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Sax states that at the level of 500 ppm, methylcyclohexane "exhibits only a very faint odor."
  2. Irritation Levels: Sax states that "this material does not cause irritation to the eyes and nose."
  3. Evaluation of Warning Properties: At concentrations within two or three times the permissible exposure limit, methylcyclohexane can be detected through its odor. Therefore, for the purposes of this guideline, 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**

Sampling and analyses may be performed by collection of methylcyclohexane 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 methylcyclohexane may be used. An analytical method for methylcyclohexane 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 methylcyclohexane.
- Clothing wet with liquid methylcyclohexane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylcyclohexane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylcyclohexane, the person performing the operation should be informed of methylcyclohexane's hazardous properties.
- Any clothing which becomes wet with liquid methylcyclohexane should be removed immediately and not reworn until the methylcyclohexane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methylcyclohexane may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methylcyclohexane should be promptly washed or showered with soap or mild detergent and water to remove any methylcyclohexane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylcyclohexane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a diluent solvent for cellulose during spray application of lacquers	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during wire- and textile-coating operations with resins and rubber	General dilution ventilation
Liberation during brush and hand application of synthetic varnishes, lacquers, and paints	General dilution ventilation; personal protective equipment
Use during manufacture of rotogravure inks	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a solvent for oils, fats, waxes, and rubber; use as a diluent in resin molding; use as a degreasing agent	General dilution ventilation; personal protective equipment
Use in industrial organic synthesis in hydroreforming process	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 methylcyclohexane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If methylcyclohexane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If methylcyclohexane soaks 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 methylcyclohexane, 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 methylcyclohexane 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 methylcyclohexane 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. Methylcyclohexane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Methylcyclohexane may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR METHYLCYCLOHEXANE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister. Any supplied-air respirator. Any self-contained breathing apparatus.
10,000 ppm or less	A gas mask with a front- or back-mounted organic vapor canister. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode. 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 Methylcyclohexanol

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: $C_7H_{14}O$
- Synonyms: Hexahydrocresols; mixture of 2-, 3-, and 4-methylcyclohexanols
- Appearance and odor: Straw-colored liquid with a weak coconut oil odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylcyclohexanol is 100 parts of methylcyclohexanol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 470 milligrams of methylcyclohexanol per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for methylcyclohexanol a Threshold Limit Value of 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylcyclohexanol can affect the body if it is inhaled, comes in contact with the eyes or skin, or swallowed. It may enter the body through the skin.

- **Effects of overexposure**

Headache and irritation of the eyes, nose, and throat may result from prolonged exposure to excessive concentrations of methylcyclohexanol. Prolonged or repeated contact of liquid methylcyclohexanol may cause a skin rash. In animal experiments methylcyclohexanol has caused drowsiness, unconsciousness, and mild liver and kidney 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 methylcyclohexanol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylcyclohexanol 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 methylcyclohexanol exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylcyclohexanol might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Methylcyclohexanol 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: Methylcyclohexanol 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: Methylcyclohexanol 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.

—Neurologic disorders: By analogy to effects observed in animals, methylcyclohexanol may adversely affect the nervous system.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylcyclohexanol vapor is a mild irritant of the eyes and mucous membranes in animals; high concentrations cause signs of narcosis. The oral LD50 in rats was approximately 2 g/kg; effects were signs of narcosis;

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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autopsy findings included congestive changes in several organs, including the liver and kidneys. Repeated daily application of large doses to the skin of rabbits caused skin irritation, weakness, tremor, narcosis, and death. Repeated daily exposure of rabbits to 503 ppm for 10 weeks caused conjunctivitis and lethargy; 230 ppm caused no effects; narcosis did not occur at the highest vapor concentration achievable at room temperature. In humans, headache and irritation of the eyes and upper respiratory tract may result from prolonged exposure to excessive concentrations. Prolonged or repeated contact of the liquid on the skin may cause dermatitis due to a defatting action.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 114.2
  2. Boiling point (760 mm Hg): 155 – 180 C (311 – 356 F)
  3. Specific gravity (water = 1): 0.92
  4. Vapor density (air = 1 at boiling point of methylcyclohexanol): 3.9
  5. Melting point: Less than –21 C (less than –6 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): Slight
  8. Evaporation rate (butyl acetate = 1): 0.02
- **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 carbon monoxide) may be released in a fire involving methylcyclohexanol.
  4. Special precautions: Methylcyclohexanol will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 65 C (149 F) (closed cup)
  2. Autoignition temperature: 296 C (565 F)
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Patty states that "methylcyclohexanol vapor in air can be detected and recognized by its odor when present to the extent of 500 ppm . . . ."
  2. Eye Irritation Level: The *Handbook of Organic Industrial Solvents* states that eye irritation does not occur until concentrations reach 500 ppm.
  3. Other Information: Patty states that 500 ppm is capable of causing upper respiratory tract irritation.
  4. Evaluation of Warning Properties: Since the odor and irritation thresholds of methylcyclohexanol are not within three times the permissible exposure limit, methylcyclohexanol is treated like 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 methylcyclohexanol 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 repeated or prolonged skin contact with liquid methylcyclohexanol.
- Clothing wet with methylcyclohexanol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylcyclohexanol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylcyclohexanol, the person performing the operation should be informed of methylcyclohexanol's hazardous properties.
- Non-impervious clothing which becomes contaminated with methylcyclohexanol should be removed promptly and not reworn until the methylcyclohexanol is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methylcyclohexanol may contact the eyes.

SANITATION

• Skin that becomes contaminated with methylcyclohexanol should be promptly washed or showered with soap or mild detergent and water to remove any methylcyclohexanol.

• Employees who handle liquid methylcyclohexanol 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 methylcyclohexanol may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in lacquers, oils, gums, waxes, and resins	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an auxiliary solvent for dry cleaning soaps in soap manufacture	Process enclosure; local exhaust ventilation; personal protective equipment
Use in textile industry as a blending agent in textile soaps; use as a degreaser; as an antioxidant in lubricants	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 methylcyclohexanol 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 methylcyclohexanol gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid methylcyclohexanol 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 methylcyclohexanol, 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 methylcyclohexanol 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 methylcyclohexanol 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 reclaimed or atomized in a suitable combustion chamber.

• Waste disposal methods:

Methylcyclohexanol 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: "Methylcyclohexanol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• *Handbook of Organic Industrial Solvents, Technical Guide No. 6* (4th ed.), American Mutual Insurance Alliance, Chicago, 1972.

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RESPIRATORY PROTECTION FOR METHYLCYCLOHEXANOL

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10,000 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 10,000 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 o-Methylcyclohexanone

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: $C_7H_{12}O$
- Synonyms: 2-Methylcyclohexanone
- Appearance and odor: Colorless liquid with a weak peppermint odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for o-methylcyclohexanone is 100 parts of o-methylcyclohexanone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 460 milligrams of o-methylcyclohexanone per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for o-methylcyclohexanone a Threshold Limit Value of 50 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

o-Methylcyclohexanone can affect the body if it is inhaled, comes in contact with the eyes or skin, or swallowed.

- **Effects of overexposure**

There are no reported effects of human exposure to o-methylcyclohexanone. In animal experiments o-methylcyclohexanone has caused drowsiness, unconsciousness, irritation of the eyes, nose, and throat, and 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 o-methylcyclohexanone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to o-methylcyclohexanone 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-methylcyclohexanone exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of o-methylcyclohexanone might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Although o-methylcyclohexanone 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 o-methylcyclohexanone 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.

—Skin disease: o-Methylcyclohexanone 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.

—Neurologic disorders: By analogy to effects observed in animals, the nervous system may be adversely affected by o-methylcyclohexanone.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

o-Methylcyclohexanone vapor irritates the eyes and mucous membranes in animals; at high concentrations it

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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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causes narcosis. Several species of animals exposed to 3500 ppm suffered marked irritation of the mucous membranes, became incoordinated after 15 minutes of exposure, and prostrate after 30 minutes. Repeated daily application to the skin of rabbits of large doses of the liquid caused irritation of the skin, tremors, narcosis, and death. Exposure of mice to 450 ppm for an unspecified time period resulted in irritation of the eyes and respiratory tract. Repeated or prolonged contact of the liquid with the skin may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 112.2
2. Boiling point (760 mm Hg): 165 C (329 F)
3. Specific gravity (water = 1): 0.93
4. Vapor density (air = 1 at boiling point of o-methylcyclohexanone): 3.9
5. Melting point: −14 C (6.8 F)
6. Vapor pressure at 20 C (68 F): 1 mm Hg (approximately)
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: None hazardous
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 o-methylcyclohexanone.
4. Special precautions: o-Methylcyclohexanone will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 47.8 C (118 F) (Closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of o-methylcyclohexanone.
2. Irritation Level: According to Patty, eye and respiratory irritation may occur below the permissible exposure limit.
3. Evaluation of Warning Properties: Through its irritant effects, o-methylcyclohexanone can be detected at 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**

An analytical method for o-methylcyclohexanone 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 repeated or prolonged skin contact with liquid o-methylcyclohexanone.
- Clothing wet with o-methylcyclohexanone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of o-methylcyclohexanone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the o-methylcyclohexanone, the person performing the operation should be informed of o-methylcyclohexanone's hazardous properties.
- Non-impervious clothing which becomes contaminated with o-methylcyclohexanone should be removed

promptly and not reworn until the o-methylcyclohexanone is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid o-methylcyclohexanone may contact the eyes.

SANITATION

• Skin that becomes contaminated with o-methylcyclohexanone should be promptly washed or showered with soap or mild detergent and water to remove any o-methylcyclohexanone.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to o-methylcyclohexanone may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in plastic industry; manufacture of lacquers and varnishes; as a co-solvent with cyclohexanone	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in leather industry; use as a rust remover	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 liquid o-methylcyclohexanone 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 o-methylcyclohexanone gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid o-methylcyclohexanone 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-methylcyclohexanone, 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-methylcyclohexanone 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 o-methylcyclohexanone 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 reclaimed or atomized in a suitable combustion chamber. o-Methylcyclohexanone 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 o-methylcyclohexanone vapors are permitted.

• Waste disposal methods:

o-Methylcyclohexanone 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: "o-Methylcyclohexanone," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR o-METHYLCYCLOHEXANONE

Condition	Minimum Respiratory Protection* Required Above 100 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.
Greater than 2500 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 Methylene Bisphenyl Isocyanate (MDI)

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: $NCOC_6H_4CH_2C_6H_4NCO$
- Synonyms: MDI; 4,4-diphenylmethane diisocyanate; methylene bis (4-phenyl isocyanate); 4,4-diisocyantodiphenylmethane
- Appearance and odor: White to light-yellow flakes with no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylene bisphenyl isocyanate is a ceiling level of 0.02 part of methylene bisphenyl isocyanate per million parts of air (ppm). This may also be expressed as 0.2 milligram of methylene bisphenyl isocyanate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylene bisphenyl isocyanate 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 methylene bisphenyl isocyanate may make a person allergic to it and produce wheezing, shortness of breath, and coughing. It may also cause irritation of the eyes and lungs, upset stomach, vomiting, possibly fever, stuffiness of the nose, sore throat, a feeling of tightness in the chest, cough, shortness of breath and wheezing. Such symptoms may be delayed up to eight hours after the person has been exposed.

2. Long-term Exposure: A person may become increasingly sensitive or allergic to methylene bisphenyl isocyanate. Chronic exposure to it may lead to permanent breathing or chest problems. Repeated or prolonged exposure of the skin to methylene bisphenyl isocyanate 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 methylene bisphenyl isocyanate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylene bisphenyl isocyanate 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 methylene bisphenyl isocyanate would be expected to be at increased risk from exposure. Examination of the eyes and respiratory tract should be stressed.

—14" x 17" chest roentgenogram: Methylene bisphenyl isocyanate may cause lung damage in humans. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Methylene bisphenyl isocyanate 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 considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Methylene bisphenyl isocyanate (MDI) vapor is a potent respiratory sensitizer. It also is a strong irritant of the eyes, mucous membranes, and skin and can cause

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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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pulmonary edema. Exposure of humans to high concentrations causes cough, dyspnea, increased secretions, and chest pain. Isocyanates cause pulmonary sensitization in susceptible individuals; should this occur, further exposure should be avoided, since extremely low levels of exposure may trigger an asthmatic episode; cross sensitization to unrelated materials probably does not occur. The liquid in contact with the eye may cause an irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 250.25
2. Boiling point (760 mm Hg): 172 C (341.6 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of methylene bisphenyl isocyanate): 8.6
5. Melting point: 37 C (98.6 F)
6. Vapor pressure at 20 C (68 F): 0.05 mm Hg
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: Temperatures above 37.8 C (100 F)
2. Incompatibilities: Avoid contact with strong alkalies, acids, and alcohol.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving methylene bisphenyl isocyanate.
4. Special precautions: Liquid methylene bisphenyl isocyanate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 202 C (395.6 F) (open cup)
2. Autoignition temperature: 240 C (464 F)
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Carbon dioxide, dry chemical, or inert gas. For large fires, water in the form of spray should be used.

- **Warning properties**

1; Odor Threshold: No quantitative information is available.

2; Irritation Levels: By analogy to TDI, which, according to Grant, causes irritation of the eyes and nose beginning at 0.05 ppm to 0.1 ppm, MDI is assumed to produce eye and nose irritation at the same levels.

3; Evaluation of Warning Properties: MDI is treated as a material with poor warning properties, for the purposes of this guideline. By analogy with TDI, MDI is assumed to produce eye and nose irritation within several times the permissible exposure limit, but the permissible exposure is a ceiling concentration.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methylene bisphenyl isocyanate. 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 methylene bisphenyl isocyanate 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 skin contact with solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate, where skin contact may occur.
- If employees' clothing may have become contaminated with methylene bisphenyl isocyanate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with methylene bisphenyl isocyanate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylene bisphenyl isocyanate from

the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylene bisphenyl isocyanate, the person performing the operation should be informed of methylene bisphenyl isocyanate's hazardous properties.

- Non-impervious clothing which becomes contaminated with methylene bisphenyl isocyanate should be removed promptly and not reworn until the methylene bisphenyl isocyanate 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 solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate contacting the eyes.

SANITATION

- Skin that becomes wet with methylene bisphenyl isocyanate should be promptly washed or showered with soap or mild detergent and water to remove any methylene bisphenyl isocyanate.
- Employees who handle solid methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate 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 methylene bisphenyl isocyanate may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during in place spraying of urethane foams	Local exhaust ventilation; respiratory protective equipment
Liberation during in place molding of urethane foams	Local exhaust ventilation; dilution ventilation
Liberation during application of polyisocyanate lacquer sealant finishes	Local exhaust ventilation; respiratory protective equipment
Liberation during shake-out and core knock-out operations at foundries using MDI-oil-base-no-bake binding systems	Local exhaust ventilation; respiratory protective equipment
Liberation during manufacture of lacquer	Process enclosure; local exhaust ventilation
Liberation during production of component chemicals for foam systems	Local exhaust ventilation; process enclosure
Liberation during casting of high-density polyurethane elastomers	Process enclosure; local exhaust ventilation
Liberation following combustion of urethane foams in fires or thermal decomposition to salvage metal inserts	Air-supply respiratory protective equipment or local exhaust ventilation
Liberation of unreacted vapor during cutting and fabricating of polyurethane foams	Local exhaust ventilation; respiratory protective equipment
Liberation during curing process; during flame lamination of fabrics	Process enclosure; local 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 methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate soak 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 methylene bisphenyl isocyanate, 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 methylene bisphenyl isocyanate or liquids containing methylene bisphenyl isocyanate 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 some-

one 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 methylene bisphenyl isocyanate 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.

• Waste disposal methods:

Methylene bisphenyl isocyanate 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 METHYLENE BISPHENYL ISOCYANATE (MDI)

Condition	Minimum Respiratory Protection* Required Above 0.02 ppm
Vapor or Particulate Concentration	
1 ppm (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.
10 ppm (100 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 10 ppm (100 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. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Methylene Chloride

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_2Cl_2
- Synonyms: Dichloromethane; methylene dichloride
- Appearance and odor: Colorless liquid with an odor like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylene chloride is 500 parts of methylene chloride per million parts of air (ppm) averaged over an eight-hour work shift, with an acceptable ceiling level of 1000 ppm and a maximum peak concentration of 2000 ppm for 5 minutes in any two-hour period. NIOSH has recommended that the permissible exposure limit be reduced to 75 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 500 ppm averaged over a 15-minute period. NIOSH further recommends that permissible levels of methylene chloride be reduced where carbon monoxide is present. The NIOSH Criteria Document for Methylene Chloride should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylene chloride 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: Methylene chloride is an anesthetic. Inhaling the vapor may cause mental confusion, light-headedness, nausea, vomiting, and headache. Continued exposure may cause increased light-headedness, staggering, unconsciousness, and death. High vapor concentrations may also cause irritation of the eyes and respiratory tract. Exposure to this chemical may make the symptoms of angina worse. Skin exposure to the liquid may cause irritation. If the liquid is held in contact with the skin, it may cause skin burns. Splashes of the liquid into the eyes may cause irritation.

2. Long-term Exposure: Prolonged or repeated exposure to methylene chloride 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 methylene chloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylene chloride 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, cardiovascular system, and blood should be stressed. Clinical impressions of the autonomic nervous system and pulmonary function should be made, with additional tests conducted where indicated.

—Skin disease: Methylene chloride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver function test: Methylene chloride causes liver damage in animals and this justifies consideration before exposing persons with impaired liver function. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Methylene chloride causes kidney damage in animals and this justifies special considera-

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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tion before exposing persons with impaired renal function.

—Cardiovascular disease: Because of reports of excessive carbon monoxide levels following exposure to methylene chloride, persons with cardiac disease may be at increased risk.

—A complete blood count: 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. Carboxyhemoglobin values should also be determined periodically, and any level above 5% should prompt an investigation of the worker and his workplace.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Methylene chloride vapor is a mild narcotic. Exposure of animals to 15,000 ppm for 7 hours was fatal. Animal experiments have shown that continuous exposure to 1,000 ppm can be lethal in 5 to 7 weeks for dogs and that fatty livers, icterus, pneumonia, and splenic atrophy developed in dogs. Cardiac arrhytmias attributed to sensitization of the myocardium have been observed following exposure to high concentrations of some chlorinated hydrocarbons, but dogs exposed to 10,000 and 20,000 ppm of methylene chloride did not show this phenomenon. In human experiments, inhalation of 500 to 1000 ppm for 1 to 2 hours resulted in lightheadedness; there was sustained elevation of carboxyhemoglobin level. High exposures have resulted in deaths in industrial situations. Lower but unknown concentrations have caused such symptoms as lightheadedness, weakness, nausea, and "drunken behavior," resulting in mistakes and accidental falls. Phosgene poisoning has been reported to occur in several cases where methylene chloride was used in the presence of an open fire. Liquid methylene chloride is irritating to the skin on repeated contact. Splashed in the eye, it is painfully irritating, but is not likely to cause serious injury.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 84.9
2. Boiling point (760 mm Hg): 39.8 C (104 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of methylene chloride): 2.9
5. Melting point: −97 C (−142 F)
6. Vapor pressure at 20 C (68 F): 350 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.32
8. Evaporation rate (butyl acetate = 1): 27.5

• **Reactivity**

1. Conditions contributing to instability: Heat and moisture
2. Incompatibilities: Contact with strong oxidizers, strong caustics, and chemically active metals such as aluminum or magnesium powder, sodium and potassium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving methylene chloride.
4. Special precautions: Liquid methylene chloride will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: None with normal test method
2. Autoignition temperature: 556 C (1033 F)
3. Flammable limits in air, % by volume: (at elevated temperatures) Lower: 12; Upper: 19
4. Extinguishant: Dry chemical, carbon dioxide, foam

• **Warning properties**

1. Odor Threshold: Different authors have reported varying odor thresholds for methylene chloride. Summer and May both report 150 ppm; Kirk-Othmer and Sax both report 25 to 50 ppm; Spector reports 320 ppm. Patty, however, states that since one can become adapted to the odor, it cannot be considered an adequate warning property.
2. Eye Irritation Level: Grant reports that methylene chloride "presents no particular hazard to the eyes." Kirk-Othmer, however, reports that "methylene chloride vapor is seriously damaging to the eyes." Sax agrees with Kirk-Othmer's statement.

The *Documentation of TLV's* states that irritation of the eyes has been observed in workers who had been exposed to concentrations up to 5000 ppm, but that neurasthenic disorders were found in 50% and digestive disturbances in 30% of the persons exposed.

3. Other Information: Gleason reports that methylene chloride may be "irritating to the respiratory tract and may produce pulmonary edema" but gives no quantitative information. The *Documentation of TLV's* reports that in one investigation, irritation of the respiratory passages was observed in workers who had been exposed to concentrations up to 5000 ppm.
4. Evaluation of Warning Properties: Since no detailed information is available relating the irritant effects of methylene chloride to air concentrations and since adaptation to the odor occurs, methylene chloride is 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 methylene chloride. 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 methylene chloride. 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 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 methylene chloride may be used. An analytical method for methylene chloride 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 methylene chloride.

• Non-impervious clothing which becomes wet with liquid methylene chloride should be removed promptly and not reworn until the methylene chloride is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methylene chloride may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methylene chloride should be promptly washed or showered with soap or mild detergent and water to remove any methylene chloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylene chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in paint and varnish removers; manufacture of aerosols; cold cleaning and ultrasonic cleaning; and as an extraction solvent for foods and furniture processing	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a cooling solvent in manufacture of cellulose acetate; in organic synthesis; and in plastics processing	Process enclosure; local exhaust ventilation
Use as a solvent in vapor degreasing of thermal switches and thermometers	Process enclosure; local exhaust ventilation
Use as a secondary refrigerant in air conditioning and scientific testing	General dilution ventilation; local exhaust ventilation; personal protective equipment

Operation	Controls
Use as an extraction solvent for edible fats, coca, butter, beer flavoring in hops, decaffeinated coffee, oleoresin manufacture, oils, waxes, perfumes, flavorings, and drugs	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent for paints, lacquers, varnishes, enamels, adhesives, rubber cements, manufacture of printed circuit boards, as a carrier for pharmaceutical tablet coatings, shrink-fitting of synthetic rubber covers, and dyeing of synthetic fibers	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 methylene chloride 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 methylene chloride gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water if the methylene chloride has not already evaporated. If methylene chloride 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 methylene chloride, 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 methylene chloride 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 methylene chloride 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.

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RESPIRATORY PROTECTION FOR METHYLENE CHLORIDE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
5000 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 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 Health Guideline for Methyl Formate

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: $HCOOCH_3$
- Synonyms: Methyl methanoate; formic acid, methyl ester
- Appearance and odor: Colorless liquid with a pleasant odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl formate is 100 parts of methyl formate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 250 milligrams of methyl formate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl formate 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: Exposure to methyl formate may cause irritation of the eyes, nose, throat, and lungs. It may also cause drowsiness and, at high levels, unconsciousness and death.

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 methyl formate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl formate 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 methyl formate exposure.

—Eye disease: Methyl formate is an eye irritant. Persons with pre-existing eye 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 methyl formate might cause exacerbation of symptoms due to its irritant properties.

—Neurological disorders: By analogy to effects observed in animals and by effects observed in humans, persons with pre-existing neurological 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**

Methyl formate vapor at high concentrations is an irritant of the eyes and respiratory tract; it also causes narcosis in animals. Exposure of guinea pigs to 10,000 ppm for 3 hours was fatal; effects were eye and nose irritation, incoordination, narcosis, and pulmonary edema. Workers exposed to the vapor of a solvent containing 30% methyl formate, in addition to ethyl formate, methyl acetate, and ethyl acetate, complained of irritation of mucous membranes, oppression in the chest, dyspnea, symptoms of central nervous system depression, and temporary visual disturbances; air concentrations were not determined. No short-term effects were noted from experimental human exposures to 1500 ppm for 1 minute.

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: 60.1
2. Boiling point (760 mm Hg): 31.7 C (89 F)
3. Specific gravity (water = 1): 0.98
4. Vapor density (air = 1 at boiling point of methyl formate): 2.1
5. Melting point: −100 C (−148 F)
6. Vapor pressure at 20 C (68 F): 476 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 30
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 formic acid and carbon monoxide) may be released in a fire involving methyl formate.
4. Special precautions: Methyl formate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −18.9 C (−2 F) (closed cup)
2. Autoignition temperature: 465 C (869 F)
3. Flammable limits in air, % by volume: Lower: 5.0; Upper: 23
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Both Summer and May report an odor threshold of 2000 ppm for methyl formate. Browning, however, states that "men exposed for 1 minute to 1500 ppm of the vapour in air noticed the odour of methyl formate . . . ." Browning states that olfactory fatigue occurs, and thus odor may not be an effective warning of exposure to dangerous concentrations.
2. Eye Irritation Level: Grant states that the vapor of methyl formate "has been found to cause no eye irritation in experimental animals at a concentration of 1500 ppm in air, but does cause some irritation at 3500 ppm."
3. Other Information: According to Grant, methyl formate in high concentrations causes nasal irritation also, but quantitative information is not given.
4. Evaluation of Warning Properties: Since the thresholds of odor and of irritation are well above the permissible exposure limit, methyl formate 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 methyl formate 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 methyl formate.
- Clothing wet with liquid methyl formate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl formate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl formate, the person performing the operation should be informed of methyl formate's hazardous properties.
- Any clothing which becomes wet with liquid methyl formate should be removed immediately and not reworn until the methyl formate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl formate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl formate should be promptly washed or showered to remove any methyl formate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl formate may occur and control methods which may be effective in each case:

Operation	Controls
Use as insecticide and larvicide for fumigating dried fruits, nuts, tobacco, cereals, and infected clothing	Personal protective equipment
Use as a general industrial solvent for greases, fatty acids, cellulose acetate, collodion, and celluloid	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for production of sulfa drugs, perfumes, dyes, military poison gases, and embalming fluid	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of methyl formate	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 methyl formate 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 methyl formate gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid methyl formate soaks 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 methyl formate, 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 methyl formate 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 methyl formate 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. Methyl formate 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 methyl formate vapors are permitted.

• Waste disposal method:

Methyl formate may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Methyl Formate," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR METHYL FORMATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3500 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.**
5000 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 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.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for 5-Methyl-3-Heptanone

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: $C_8H_{16}O$
- Synonyms: Ethyl sec-amyl ketone; ethyl amyl ketone; amyl ethyl ketone
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 5-methyl-3-heptanone is 25 parts of 5-methyl-3-heptanone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 130 milligrams of 5-methyl-3-heptanone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

5-Methyl-3-heptanone 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: 5-Methyl-3-heptanone may irritate the eyes, nose, and throat, and may cause headache, and dizziness. At very high air concentrations, the vapor may cause unconsciousness in a short time. *2. Long-term Exposure:* Prolonged or repeated skin contact may cause dryness and 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 5-methyl-3-heptanone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 5-methyl-3-heptanone 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 5-methyl-3-heptanone exposure.

—Kidney disease: Although 5-methyl-3-heptanone 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 5-methyl-3-heptanone might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although 5-methyl-3-heptanone 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: 5-Methyl-3-heptanone 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**

There is local irritation of tissues by solvent effect of 5-methyl-3-heptanone on lipids. Central nervous system depression may occur on exposure to high concentrations, producing narcosis. No chronic effects are reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 128

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

2. Boiling point (760 mm Hg): 159 C (318 F)
3. Specific gravity (water = 1): 0.82
4. Vapor density (air = 1 at boiling point of 5-methyl-3-heptanone): 4.4
5. Melting point: −57 C (−70 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.26
8. Evaporation rate (butyl acetate = 1): 0.26

• **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 5-methyl-3-heptanone.
4. Special precautions: None

• **Flammability**

1. Flash point: 43.3 C (110 F) (Tag closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical, or foam

• **Warning properties**

1. Odor Threshold: The *Documentation of TLV's* reports that Shell Chemical Corporation determined the odor threshold to be 6 ppm.
2. Irritation Levels: According to the *Documentation of TLV's*, "Shell Chemical Corporation presented the following observations in respect to sensory responses by unconditioned personnel during or following 5-minute exposures to the vapor: . . . 50% Threshold, eye irritation 50 ppm 50% Threshold, nose irritation 50 ppm"

The irritation of the nose and eyes is, according to the *Documentation of TLV's*, transient.

3. Evaluation of Warning Properties: Since 5-methyl-3-heptanone has an odor threshold which is lower than 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**

Sampling and analyses may be performed by collection of 5-methyl-3-heptanone 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 5-methyl-3-heptanone may be used. An analytical method for 5-methyl-3-heptanone 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).
number PB 245 851).

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 protect any area of the body which may come in contact with liquid 5-methyl-3-heptanone.

• Clothing wet with 5-methyl-3-heptanone should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 5-methyl-3-heptanone from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 5-methyl-3-heptanone, the person performing the operation should be informed of 5-methyl-3-heptanone's hazardous properties.

• Non-impervious clothing which becomes wet with 5-methyl-3-heptanone should be removed promptly and not reworn until the 5-methyl-3-heptanone is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid 5-methyl-3-heptanone may contact the eyes.

SANITATION

• Skin that becomes wet with 5-methyl-3-heptanone should be promptly washed or showered to remove any 5-methyl-3-heptanone.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 5-methyl-3-heptanone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray application of resinous and lacquer surface coatings	Local exhaust ventilation; personal protective equipment
Liberation during subdivision of large quantities of ethyl amyl ketone or compounds containing it	General dilution ventilation; personal protective equipment
Use in preparation of perfumes	Local exhaust ventilation; personal protective equipment
Use as a specialized solvent in cleaning operations	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 5-methyl-3-heptanone 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 5-methyl-3-heptanone gets on the skin, promptly flush the contaminated skin with water. If 5-methyl-3-heptanone soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is evidence of skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of 5-methyl-3-heptanone, 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 5-methyl-3-heptanone 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 5-methyl-3-heptanone 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. 5-Methyl-3-heptanone 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 5-methyl-3-heptanone vapors are permitted.

• Waste disposal methods:

5-Methyl-3-heptanone 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.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Ethyl sec-Amyl Ketone," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR 5-METHYL-3-HEPTANONE

Condition	Minimum Respiratory Protection* Required Above 25 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.
3000 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 3000 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 MONOMETHYL HYDRAZINE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about monomethyl hydrazine 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:** CH_6N_2
- **Structure:** CH_3NHNH_2
- **Synonyms:** Hydrazomethane, 1-methyl hydrazine, methyl hydrazine, MMH
- **Identifiers:** CAS 60-34-4; RTECS MV5600000; DOT 1244, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Colorless liquid with a strong ammonia-like odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 46.09
2. Boiling point (at 760 mmHg): 87.5°C (189°F)
3. Specific gravity (water = 1): 0.874
4. Vapor density (air = 1 at boiling point of monomethyl hydrazine): 1.59
5. Melting point: -52.4°C (-61.6°F)
6. Vapor pressure: At 20°C (68°F): 36.0 mmHg; at 25°C (77°F), 49.6 mmHg
7. Soluble in water
8. Evaporation rate (butyl acetate = 1): 1.5
9. Saturation concentration in air (approximate) at 25°C (77°F): 6.5% (65,300 ppm)
10. Ionization potential: 7.67 eV

- **Reactivity**

Incompatibilities: Monomethyl hydrazine is a highly reactive reducing agent, and contact with oxides of iron or copper and with manganese, lead, copper, or their alloys can lead to fires and explosions.

Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving monomethyl hydrazine.

Caution: Monomethyl hydrazine will attack cork, some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -8.3°C (17°F) (closed cup)
2. Autoignition temperature: 194°C (382°F)
3. Flammable limits in air, % by volume: Lower, 2.5; upper, 92
4. Extinguishant: Alcohol foam, dry chemical, or large quantities of coarse water spray
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Monomethyl hydrazine may ignite spontaneously when spread on a large surface or when in air and in contact with porous materials such as soil, asbestos, wood, or cloth or with oxidants such as hydrogen peroxide or nitric acid.

- **Warning properties**

1. Odor threshold: 1-3 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 monomethyl hydrazine is 0.2 parts of monomethyl hydrazine per million parts of air (ppm) [0.35 milligrams of monomethyl hydrazine per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded (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 monomethyl hydrazine 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

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Division of Standards Development and Technology Transfer

0.04 ppm (0.08 mg/m³) as a ceiling concentration determined in any 120-minute sampling period. The NIOSH REL represents the lowest reliably detectable level by NIOSH-validated methods. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated monomethyl hydrazine as an A2 substance (suspected human carcinogen) having an assigned threshold limit value ceiling (TLV®-C), the concentration that should not be exceeded during any part of the working exposure, of 0.2 ppm (0.35 mg/m³) (Skin) (Table 1).

Table 1.—Occupational exposure limits for monomethyl hydrazine

	Exposure limits ppm	mg/m³
OSHA PEL		
Ceiling (Skin)*	0.2	0.35
NIOSH REL (Ca)†		
Ceiling (120 min)	0.04	0.08
ACGIH TLV® (A2)§		
Ceiling (Skin)	0.2	0.35

* (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

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

• Summary of toxicology

Effects on animals: Acute inhalation of monomethyl hydrazine by dogs caused respiratory irritation, pulmonary hemorrhage and edema, central nervous system stimulation, and convulsions; acute subcutaneous injection in dogs caused damage to the kidneys (including hemoglobinuria, hyaline droplet degeneration, and severe renal epithelial damage). Subchronic inhalation of monomethyl hydrazine by dogs, monkeys, rats, or mice produced nose and eye irritation, diarrhea, rapid respiration, deficient oxygenation of the blood (cyanosis), impaired muscular coordination (ataxia), tremors, convulsions, blood disorders (including significant hemolysis and hemolytic anemia), increased storage of iron in the body (hemosiderosis), and reduced bile flow (cholestasis). Chronic oral administration of monomethyl hydrazine to mice produced lung tumors; hamsters similarly exposed developed liver cancer.

• Signs and symptoms of exposure

Short-term (acute): Monomethyl hydrazine can cause irritation of the eyes and respiratory tract, nausea, diarrhea, 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 monomethyl hydrazine, 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, liver, kidneys, and hematopoietic (blood-cell-forming), 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). There is little information available on the risk to a worker with a history of hemolytic anemia. The physician should obtain a complete blood cell count and baseline tests for red blood cell hemolysis.

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 monomethyl hydrazine 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 liver, kidneys, and hematopoietic and respiratory systems. The physician should obtain baseline values for liver function tests. Mild non-hemolytic anemia (e.g., mild iron-deficiency anemia) is not a contraindication for placement in a job with a potential for exposure to monomethyl hydrazine.

• **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 monomethyl hydrazine. 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 eyes, liver, kidneys, and hematopoietic, respiratory, 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 ATS: standardized questionnaires and lung function tests.

• **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 monomethyl hydrazine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of monomethyl hydrazine. 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 120-minute sample or a series of consecutive samples that total 120 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 monomethyl hydrazine vapors with sulfuric-acid-coated silica gel tubes and analyzing by gas chromatography. Direct-reading devices calibrated to measure monomethyl hydrazine may also be used if available. A detailed sampling and analytical method for monomethyl hydrazine may be found in the *NIOSH Manual of Analytical Methods* (method number 248).

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 monomethyl hydrazine.

SANITATION

Clothing which is contaminated with monomethyl hydrazine 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 monomethyl hydrazine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of monomethyl hydrazine'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 monomethyl hydrazine 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 monomethyl hydrazine 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 monomethyl hydrazine 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 monomethyl hydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If monomethyl hydrazine 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.

Table 2.—Operations and methods of control for monomethyl hydrazine

Operations	Controls
During use in the preparation and handling of liquid rocket propellants; during use as a chemical intermediate for the synthesis of pesticides	Process enclosure, local exhaust ventilation, personal protective equipment
During use in polymer technology and in miscellaneous processes such as electroplating, etching, and photographic processing	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture and distribution of monomethyl hydrazine; during maintenance of storage containers	Process enclosure, local exhaust ventilation, personal protective equipment

• **Skin exposure**

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

If monomethyl hydrazine gets on the skin, wash it immediately with soap and water. If monomethyl hydrazine 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 monomethyl hydrazine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Small quantities of liquids containing monomethyl hydrazine may be flushed with water; the waste water may then be collected in open holding tanks. Concentrations less than 2% can be oxidized by slowly adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach.
4. Large quantities of liquids containing monomethyl hydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Monomethyl hydrazine should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.

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 monomethyl hydrazine

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 appropriate escape-type self-contained breathing apparatus

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

Occupational Health Guideline for Methyl Iodide*

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_3I
- Synonyms: Iodomethane
- Appearance: Colorless liquid which turns yellow, red, and brown on exposure to light and moisture.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl iodide is 5 parts of methyl iodide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 28 milligrams of methyl iodide per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for methyl iodide from 5 ppm to 2 ppm and has classified it as having a carcinogenic potential for man.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl iodide 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: Methyl iodide may cause nausea and vomiting, diarrhea, dizziness, slurred speech, visual disturbances, staggering, shaking, irritability, drowsiness, coma, and death. It may irritate the eyes and lungs. Contact with the liquid may cause irritation and blistering of the skin.

2. Long-term Exposure: Prolonged overexposure to methyl iodide 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 methyl iodide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl iodide 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 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**

Methyl iodide vapor is an acute neurotoxin and possible pulmonary irritant. In mice, the LC50 for 57 minutes' exposure was 900 ppm; the minimum fatal dose with 24-hour exposure was 75 ppm. A chemical worker accidentally exposed to the vapor developed giddiness, diarrhea, sleepiness, and irritability, with recovery in a week; when re-exposed 3 months later, he experienced drowsiness, vomiting, pallor, incoordination, slurred speech, muscular twitching, oliguria, coma, and death. At autopsy there was bronchopneumonia and pulmonary hemorrhages, with accumulation of combined iodine in the brain. Experimental application of the liquid to human skin produced a stinging sensation and slight reddening in 10 minutes; after 6 hours' contact there was spreading erythema with later formation of vesicles. One report mentions the production of sarcomas in 15 of 24 rats of BD strain arising from the subcutaneous injection of methyl iodide in an oil solution, but the report is fragmentary.

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

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 142
  2. Boiling point (760 mm Hg): 42.5 C (108 F)
  3. Specific gravity (water = 1): 2.3
  4. Vapor density (air = 1 at boiling point of methyl iodide): 4.9
  5. Melting point: −66 C (−87 F)
  6. Vapor pressure at 20 C (68 F): 375 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 2
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat, light, and moisture
  2. Incompatibilities: Methyl iodide reacts with strong oxidizing agents.
  3. Hazardous decomposition products: Toxic gases and vapors (such as iodine and hydrogen iodide) may be released when methyl iodide decomposes.
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Although methyl iodide is known to have a sweet, ethereal odor, no quantitative data are available on the odor threshold. Methyl iodide is treated as a material with poor warning properties.

According to Grant, concentrations of methyl iodide of 4300 to 14,620 ppm caused immediate irritation of the eyes and lacrimation in mice, but 860 ppm for 10 minutes caused no 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 methyl iodide vapors using an adsorption tube with subsequent desorption with toluene and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl iodide may be used. An analytical method for methyl iodide 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 methyl iodide.
- Non-impervious clothing which becomes contaminated with liquid methyl iodide should be removed immediately and not reworn until the methyl iodide is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl iodide may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl iodide should be immediately washed or showered with soap or mild detergent and water to remove any methyl iodide.
- Employees who handle liquid methyl iodide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.
- Eating and smoking should not be permitted in areas where liquid methyl iodide is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl iodide may occur and control methods which may be effective in each case:

Operation	Controls
Use as a methylating agent in organic synthesis; use as a laboratory reagent; use in academic laboratory courses in organic chemistry	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an insecticidal fumigant on scale insects and beetles	Process enclosure; general dilution ventilation; personal protective equipment
Use in analytical chemistry laboratories (test for pyridine, evaluating type of sulfur linkage in vulcanized rubber)	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 methyl iodide gets into the eyes, wash eyes promptly 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 methyl iodide gets on the skin, immediately flush the contaminated skin using soap or mild detergent and water. If methyl iodide soaks through the clothing, remove the clothing immediately and flush 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 methyl iodide, 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 methyl iodide 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 methyl iodide 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.

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* SPECIAL NOTE

Methyl iodide appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980). 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 METHYL IODIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
800 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 800 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 Methyl Isobutyl Carbinol

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: $(CH_3)_2CHCH_2CHOHCH_3$
- Synonyms: Methyl amyl alcohol; 4-methyl-2-pentanol; MIBC
- Appearance and odor: Colorless liquid with a mild odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl isobutyl carbinol is 25 parts of methyl isobutyl carbinol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 100 milligrams of methyl isobutyl carbinol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl isobutyl carbinol can affect the body if it is swallowed, is inhaled, or comes in contact with the eyes or skin.

- **Effects of overexposure**

Overexposure to methyl isobutyl carbinol may cause eye and skin irritation. The overexposed person may also experience headache and drowsiness.

- **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 methyl isobutyl carbinol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl isobutyl carbinol 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 methyl isobutyl carbinol exposure.

—Skin disease: Methyl isobutyl carbinol 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 methyl isobutyl carbinol 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 methyl isobutyl carbinol 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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Only limited observations of the effects of methyl isobutyl carbinol have been reported, but exposure of rats to 2000 ppm for 8 hours is fatal, while 1000 ppm is not. The most important effects of methyl isobutyl carbinol are narcosis and eye irritation. Unacclimated volunteer subjects exposed to 50 ppm vapor had eye irritation. Chronic systemic effects have not been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 102
  2. Boiling point (760 mm Hg): 132 C (269 F)
  3. Specific gravity (water = 1): 0.8

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

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Occupational Safety and Health Administration

4. Vapor density (air = 1 at boiling point of methyl isobutyl carbinol): 3.5
5. Melting point: −90 C (−130 F)
6. Vapor pressure at 20 C (68 F): 3.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
8. Evaporation rate (butyl acetate = 1): 0.27

• 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 methyl isobutyl carbinol.
4. Special precautions: Methyl isobutyl carbinol will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: 41 C (106 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 5.5
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

• Warning properties

1. Odor Threshold: The *Documentation of TLV's* states that Silverman and associates observed that human subjects did not find the odor objectionable at 50 ppm.
2. Eye Irritation: According to the *Documentation of TLV's*, Silverman and associates found that human subjects experienced eye irritation at 50 ppm.
3. Evaluation of Warning Properties: Since eye irritation occurs at a level only twice the permissible exposure limit, this substance is considered to have 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 methyl isobutyl carbinol 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 methyl isobutyl carbinol may be used. An analytical method for methyl isobutyl carbinol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, field, Virginia 22161, under the title "NIOSH Analyt-

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 methyl isobutyl carbinol.

• Clothing wet with liquid methyl isobutyl carbinol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl isobutyl carbinol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl isobutyl carbinol, the person performing the operation should be informed of methyl isobutyl carbinol's hazardous properties.

• Non-impervious clothing which becomes wet with liquid methyl isobutyl carbinol should be removed promptly and not reworn until the methyl isobutyl carbinol is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl isobutyl carbinol may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methyl isobutyl carbinol should be promptly with soap or mild detergent and water washed or showered to remove any methyl isobutyl carbinol.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl isobutyl carbinol may occur

and control methods which may be effective in each case:

Operation	Controls
Liberation during application of nitrocellulose lacquers and other coatings; application of hot-spray lacquers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an extractant in dewaxing of mineral oils; use as a frother in froth flotation of various minerals, especially copper; use as an extractant in manufacture of antibiotics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during preparation of brake fluids; during preparation of lubricant additives	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in synthesis of surfactants; use in preparation of lubricating oil additives	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 methyl isobutyl carbinol 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 methyl isobutyl carbinol gets on the skin, promptly wash the contaminated skin with water. If methyl isobutyl carbinol soaks through the clothing, remove the clothing promptly and flush the skin with water. If there is skin irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of methyl isobutyl carbinol, 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 methyl isobutyl carbinol 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 methyl isobutyl carbinol 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. Methyl isobutyl carbinol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Methyl isobutyl carbinol 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 METHYL ISOBUTYL CARBINOL

Condition	Minimum Respiratory Protection* Required Above 25 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 Health Guideline for Methyl Isocyanate

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_3NCO
- Synonyms: None
- Appearance and odor: Colorless liquid with a sharp odor that causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl isocyanate is 0.02 part of methyl isocyanate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.05 milligram of methyl isocyanate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl isocyanate 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**

Inhalation of methyl isocyanate vapors may cause irritation of the eyes, nose, throat, and lungs. Cough, shortness of breath, increased phelgm and chest pain may be present. The liquid splashed in the eyes may cause permanent damage. The liquid splashed on the skin may cause irritation. Exposure to methyl isocyanate may cause a person to become allergic to it so that extremely low levels of exposure may cause an asthmatic attack.

- **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 methyl isocyanate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl isocyanate 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 methyl isocyanate would be expected to be at increased risk from exposure. 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: Methyl isocyanate causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Methyl isocyanate 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 by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Methyl isocyanate vapor is an intense lacrimator and irritates the eyes, mucous membranes, and skin. It can cause pulmonary irritation and sensitization. In rats exposed for 4 hours, the LC50 was 5 ppm; effects were injury to the lungs and subsequent pulmonary edema. Exposure of humans to high concentrations can cause cough, dyspnea, increased secretions, and chest pain. Isocyanates cause pulmonary sensitization in susceptible individuals; should this occur, further exposure should be avoided, since extremely low levels of expo-

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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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sure may trigger an asthmatic episode; cross sensitization to unrelated materials probably does not occur. Experimental exposure of four human subjects for 1 to 5 minutes caused the following effects: 0.4 ppm, no effects; 2 ppm, lacrimation, irritation of the nose and throat; 4 ppm, symptoms of irritation more marked; 21 ppm, unbearable irritation of eyes, nose, and throat. A cotton plug saturated with the liquid was applied to the ear of a rabbit for 30 minutes and caused erythema, edema, necrosis, and perforation; a few drops of the liquid on the ear of a rabbit caused destruction of tissue. The liquid in contact with the eye may cause permanent damage.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 57.1
2. Boiling point (760 mm Hg): 39 C (102 F)
3. Specific gravity (water = 1): 0.96
4. Vapor density (air = 1 at boiling point of methyl isocyanate): 2.0
5. Melting point: −80 C (−112 F)
6. Vapor pressure at 20 C (68 F): 348 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 6.7 (reacts slowly)
8. Evaporation rate (butyl acetate = 1): 26.8

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause methyl isocyanate to polymerize and burst container.
2. Incompatibilities: Contact with water causes formation of carbon dioxide and methylamine gases. The reaction is much more rapid in the presence of acids, alkalies, and amines. Contact with iron, tin, copper (or salts of these elements) and with certain other catalysts (such as triphenylarsenic oxide, triethylphosphine, and tributyltin oxide) may cause violent polymerization.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving methyl isocyanate.
4. Special precautions: Methyl isocyanate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Less than −18 C (0 F) (open cup)
2. Autoignition temperature: 535 C (995 F)
3. Flammable limits in air, % by volume: Lower: 5.3; Upper: 26
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: The *Documentation of TLV's* states that humans exposed to 0.4 ppm methyl isocyanate for periods up to 5 minutes could not detect the odor. Even at a concentration of 2 ppm, the odor was not perceived.
2. Irritation Levels: At a concentration of 0.4 ppm, eye, nose, and throat irritation was not experienced by human subjects who were exposed for periods up to 5 minutes. The *Documentation of TLV's* states that "at 2 ppm no odor was detected, but the subjects experienced irritation and lacrimation. At 4 ppm the symptoms of irritation were more marked. Exposure was unbearable at 21 ppm."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds of methyl isocyanate are not within 3 times the permissible exposure limit, for the purposes of this guideline, methyl isocyanate 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 methyl isocyanate 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 methyl isocyanate.

• Clothing wet with liquid methyl isocyanate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl isocyanate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl isocyanate, the person performing the operation should be informed of methyl isocyanate's hazardous properties.

• If employees' clothing has had any possibility of being contaminated with liquid methyl isocyanate, employees should change into uncontaminated clothing before leaving the work premises.

• Any clothing which becomes wet with and non-impervious clothing which becomes contaminated with liquid methyl isocyanate should be removed immediately and not reworn until the methyl isocyanate 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 methyl isocyanate contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid methyl isocyanate, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid methyl isocyanate should be immediately washed or showered to remove any methyl isocyanate.

• Employees who handle liquid methyl isocyanate 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 methyl isocyanate may occur and control methods which may be effective in each case:

Operation	Controls
Use as a cross-linking agent; additive to adhesives in polymer technology; use in organic synthesis	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 methyl isocyanate 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 liquid methyl isocyanate gets on the skin, immediately flush the contaminated skin with large amounts of water. If liquid methyl isocyanate soaks through the clothing, remove the clothing immediately and flush the skin with large amounts of water. If irritation persists after washing, get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of methyl isocyanate, 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 methyl isocyanate 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 methyl isocyanate 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. Methyl isocyanate 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 methyl isocyanate vapors are permitted.

• Waste disposal method:

Methyl isocyanate may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR METHYL ISOCYANATE

Condition	Minimum Respiratory Protection* Required Above 0.02 ppm
Vapor Concentration	
0.2 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1ppm 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.
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	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 METHYL MERCAPTAN

INTRODUCTION

This guideline summarizes pertinent information about methyl 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:** CH_4S
- **Structure:** CH_3—SH
- **Synonyms:** Mercaptomethane, methanethiol, methyl sulfhydrate, thiomethyl alcohol
- **Identifiers:** CAS 74-93-1; RTECS PB4375000; DOT 1064, label required: "Flammable Gas"
- **Appearance and odor:** Colorless gas with an odor like decaying cabbage

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 48.11
2. Boiling point (at 760 mmHg): 5.96°C (40.4°F)
3. Specific gravity (water = 1): 0.8665
4. Vapor density (air = 1 at boiling point of methyl mercaptan): 1.66
5. Melting point: -123°C (-190°F)
6. Vapor pressure at 20°C (68°F): 1,276 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 2.4
8. Ionization potential: 9.44 eV

- **Reactivity**

1. Incompatibilities: Strong oxidizing agents. Elevated temperature may generate high internal pressure and cause containers to burst.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., sulfur dioxide and carbon monoxide) may be released in a fire involving methyl mercaptan.
3. Caution: Liquid methyl mercaptan will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -18°C (0°F) (open cup)
2. Flammable limits in air, % by volume: Lower, 3.9; upper, 21.8
3. Extinguishant: Carbon dioxide, dry chemicals, or alcohol foam
4. Class IA Flammable Liquid (29 CFR 1910.106), Flammability Rating 4 (NFPA)

- **Warning properties**

1. Odor threshold: 1 ppb
2. Evaluation of warning properties for respirator selection: Because of its odor, methyl 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 methyl mercaptan is 10 parts of methyl mercaptan per million parts of air (ppm) [20 milligrams of methyl mercaptan per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.5 ppm (1.0 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®) is 0.5 ppm (1 mg/m^3) as a time-weighted average (TWA) concentration for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for methyl mercaptan

	Exposure limits	
	ppm	mg/m^3
OSHA PEL ceiling	10	20
NIOSH REL ceiling (15 min)	0.5	1.0
ACGIH TLV® TWA	0.5	1.0

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HEALTH HAZARD INFORMATION

• Routes of exposure

Methyl mercaptan may cause adverse health effects following exposure via inhalation or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of methyl mercaptan by rats and mice caused restlessness, increased respiration, muscular weakness progressing to paralysis, convulsions, respiratory depression, deficient oxygenation of the blood (cyanosis), and death due to respiratory paralysis. Subchronic inhalation of methyl mercaptan by monkeys, rats, and mice caused altered blood chemistries in all three species, pulmonary edema in monkeys, and persistent hepatitis and cellular changes of the liver, lungs, and kidneys in mice.

2. *Effects on humans:* An accidental industrial exposure of a worker to methyl mercaptan caused elevated blood pressure, severe hemolytic anemia, methemoglobinemia, deep coma, and death due to pulmonary embolus 28 days following exposure.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to methyl mercaptan can cause headache, dizziness, staggered gait, nausea, vomiting, pulmonary irritation, expiratory wheezing, rapid heart beat (tachycardia), rigidity of the arms and legs, bluish discoloration of the skin and mucous membranes (cyanosis), and irritation of the eyes and mucous membranes.

2. *Long-term (chronic):* Low-level exposure to methyl mercaptan can cause 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 methyl 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 risks. These should concentrate on the function and integrity of the skin 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 methyl 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 skin and 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 methyl 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 skin 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.

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling concentration evaluation

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of methyl 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**

There are no NIOSH-validated sampling and analytical methods for methyl mercaptan. Direct reading devices calibrated to measure methyl mercaptan may be used if available.

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 methyl mercaptan.

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

SANITATION

Clothing which is contaminated with liquid methyl 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 methyl mercaptan from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of methyl 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 methyl 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 methyl 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 methyl 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 methyl mercaptan

Operations	Controls
During use in the manufacture and processing of methyl mercaptan and methionine; during use as a catalyst or activator; during use in wood processing	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use in the synthesis of chemical intermediates for the manufacture of resins, plastics, insecticides, and pressure-sensitive and oil-resistant adhesives	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as an odorant and warning agent in natural gas; during use in jet fuels; during the cleaning and maintenance of storage containers	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 methyl mercaptan, an eye-wash fountain should be provided within the immediate work area for emergency use.

If methyl 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 methyl mercaptan, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If methyl mercaptan gets on the skin, wash it immediately with soap and water. If methyl 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 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 methyl mercaptan is spilled or leaked, the following steps should be taken:

1. If methyl mercaptan is in the gaseous form, stop the flow of gas. If the source of the 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.
2. Remove all ignition sources.
3. Ventilate area of spill or leak.
4. For small quantities of liquids containing methyl 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 duct work is free from methyl mercaptan vapors. Burn the paper in a suitable location away from combustible material.
5. Large quantities of liquids containing methyl mercaptan may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. Methyl mercaptan should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
6. Liquids containing methyl 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 methyl 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 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)
	Any supplied-air respirator with a tight-fitting facepiece and operated in a continuous flow mode
Less than or equal to 400 ppm	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 400 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 0.5 ppm (1.0 mg/m³) (ceiling).

Occupational Health Guideline for Methyl Methacrylate

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: $CH_2=C(CH_3)COOCH_3$
- Synonyms: Methacrylic acid, methyl ester
- Appearance and odor: Colorless liquid with an acrid, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl methacrylate is 100 parts of methyl methacrylate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 410 milligrams of methyl methacrylate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl methacrylate can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methyl methacrylate may cause irritation of the nose, throat, skin, and eyes. It may also cause drowsiness and, at very high levels, perhaps unconsciousness.

2. Long-term Exposure: Prolonged exposure 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 methyl methacrylate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl methacrylate 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 methyl methacrylate exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methyl methacrylate might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Methyl methacrylate 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 methyl methacrylate 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 methyl methacrylate 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**

The main toxic effect of methyl methacrylate is irritation of the respiratory tract by exposure to the vapor of the monomer. Rabbits exposed to 13,500 ppm for 3 hours died. Dust generated from the solid polymer is also irritating. Application to the eyes of rabbits caused irritation requiring several days for recovery. Dental technicians molding the polymer by hand developed dermatitis.

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): 100 C (212 F)
3. Specific gravity (water = 1): 0.95
4. Vapor density (air = 1 at boiling point of methyl methacrylate): 3.6
5. Melting point: −48 C (−54 F)
6. Vapor pressure at 20 C (68 F): 35 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
8. Evaporation rate (butyl acetate = 1): 3.1

- **Reactivity**

1. Conditions contributing to instability: Heat/and or lack of appropriate inhibitor concentration can cause methyl methacrylate to polymerize violently and burst container.
2. Incompatibilities: Contact with nitrates, oxidizing materials, including peroxides and other initiators of polymerization, 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 methyl methacrylate.
4. Special precautions: Inhibitors do not function in absence of air, so inert gas blankets should not be used.

- **Flammability**

1. Flash point: 10 C (50 F) (closed cup)
2. Autoignition temperature: 421 C (790 F)
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.2
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for methyl methacrylate of 0.21 ppm.
2. Eye Irritation Level: According to Grant, "on application to rabbit eyes it (methyl methacrylate) has caused irritation requiring several days for recovery. The TLV is recommended "to protect against discomfort from irritation."
3. Other Information: According to the *Documentation of TLV's*, some "investigators noted irritation at 170 to 250 ppm, but workers tolerated without complaint levels approximating 200 ppm . . . . It was the opinion of men in the field that 100 ppm could be tolerated continuously for 8 hours without discomfort."
4. Evaluation of Warning Properties: Since its odor threshold is below the permissible exposure limit, and since irritation occurs within 3 times the permissible exposure limit, methyl methacrylate 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 methyl methacrylate 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 methyl methacrylate may be used. An analytical method for methyl methacrylate 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 liquid methyl methacrylate.
- Clothing wet with liquid methyl methacrylate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

methyl methacrylate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl methacrylate, the person performing the operation should be informed of methyl methacrylate's hazardous properties.

- Any clothing which becomes wet with liquid methyl methacrylate should be removed immediately and not reworn until the methyl methacrylate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid methyl methacrylate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methyl methacrylate should be promptly washed or showered with soap or mild detergent and water to remove any methyl methacrylate.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl methacrylate may occur and control methods which may be effective in each case:

Operation	Controls
Use during casting of acrylic sheets	Local exhaust ventilation; personal protective equipment
Use during molding of acrylic sheets or polymethacrylate powders	Local exhaust ventilation; general dilution ventilation
Use during spray application of unsaturated polyester resins (surface coatings or structural components); use during brush or roller applications of unsaturated polyester resins (surface coatings or structural components)	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of methyl methacrylate resins for surface coatings; during polymerization to produce molding and extruding powders	Process enclosure; general dilution ventilation
Liberation during production of synthetic fibers; during manufacture of unsaturated polyester resins	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during dye molding of articles from polyester resins; during production of emulsion polymers for use in adhesives, sealants, fabrics, sizes, leather finishes, paper coatings, polishes, etc.; during machining of articles from resins (acrylic plastics)	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 methyl methacrylate 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 methyl methacrylate gets on the skin, promptly flush the contaminated skin with water. If methyl methacrylate soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of methyl methacrylate, 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 methyl methacrylate 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 methyl methacrylate 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. Methyl methacrylate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Methyl methacrylate may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill in an area where the odor will not be objectionable.
2. By atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR METHYL METHACRYLATE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
4000 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 4000 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-Methyl Styrene

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: $C_6H_5C(CH_3)=CH_2$ or C_9H_{10}
- Synonyms: 1-Methyl-1-phenylethylene; AMS
- Appearance and odor: Colorless liquid with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for alpha-methyl styrene is a ceiling level of 100 parts of alpha-methyl styrene per million parts of air (ppm). This may also be expressed as 480 milligrams of alpha-methyl styrene per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for alpha-methyl styrene from 100 ppm to 50 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

alpha-Methyl styrene 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: alpha-Methyl styrene may cause irritation of the eyes, nose, and throat. The overexposed person may experience drowsiness.

2. Long-term Exposure: Prolonged exposure may produce 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 alpha-methyl styrene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to alpha-methyl styrene 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-methyl styrene exposure.

—Skin disease: alpha-Methyl styrene can cause dermatitis on prolonged exposure. Persons 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 alpha-methyl styrene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Kidney disease: Although alpha-methyl styrene 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 alpha-methyl styrene 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 alpha-methyl styrene causes slight irritation of the eyes, upper respiratory tract, and skin. With prolonged and repeated contact, there may be depression of the central nervous system.

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: 118
2. Boiling point (760 mm Hg): 165 C (329 F)
3. Specific gravity (water = 1): 0.92
4. Vapor density (air = 1 at boiling point of alpha-methyl styrene): 4.1
5. Melting point: −23 C (−9 F)
6. Vapor pressure at 20 C (68 F): 1.9 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with oxidizing agents (including peroxides and halogens) may cause fires and explosions. Also, avoid contact with catalysts for vinyl polymerization and catalysts for ionic polymerization, such as aluminum or iron chloride.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving alpha-methyl styrene.
4. Special precautions: None

- **Flammability**

1. Flash point: 54 C (129 F) (closed cup)
2. Autoignition temperature: 574 C (1066 F)
3. Flammable limits in air, % by volume: Lower: 1.9; Upper: 6.1
4. Extinguishant: Carbon dioxide, dry chemical, or foam.

- **Warning properties**

1. Odor Threshold: According to the *Documentation of TLV's*, "four human subjects exposed to a concentration of 200 ppm of alpha-methyl styrene reported definite unpleasant odor . . . after two minutes." This concentration is not necessarily the odor threshold.
2. Eye Irritation Level: The *Documentation of TLV's* also notes that at 200 ppm human subjects experienced eye irritation. This concentration is not necessarily the threshold of eye irritation.
3. Evaluation of Warning Properties: alpha-Methyl styrene can be detected at a concentration less than twice the permissible exposure limit. Even though the permissible exposure limit is a ceiling concentration, alpha-methyl styrene is still treated as a material with adequate warning properties, since the ceiling appears to have been established to avoid irritant effects. The *Documentation of TLV's* gives the following quote of Dow Chemical Company: "We suggest, therefore, an Industrial Hygiene Standard of 200 ppm based on toxicity. For engineering purposes, we suggest that the vapor concentration be controlled to 100 ppm alpha-methyl styrene in order to minimize complaints of exposed persons."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of alpha-methyl styrene. 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 alpha-methyl styrene 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 alpha-methyl styrene may be used. An analytical method for alpha-methyl styrene 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 alpha-methyl styrene.
- Clothing wet with liquid alpha-methyl styrene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

alpha-methyl styrene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the alpha-methyl styrene, the person performing the operation should be informed of alpha-methyl styrene's hazardous properties.

• Non-impervious clothing which becomes contaminated with liquid alpha-methyl styrene should be removed promptly and not reworn until the alpha-methyl styrene is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid alpha-methyl styrene may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid alpha-methyl styrene should be promptly washed or showered with soap or mild detergent and water to remove any alpha-methyl styrene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to alpha-methyl styrene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture of styrene-butadiene rubber	General dilution ventilation
Liberation during spray application of specialized alpha-methyl-styrene-polyester surface coatings	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during manufacture of high-impact acrylonitrile-butadiene-styrene plastics; during manufacture of specialized alpha-methyl-styrene-polyester and alkyd surface coating resins; during manufacture of certain plasticizers in varnishes, adhesives, and plastics; during manufacture of carbolic acid with cumene peroxidation process	General dilution ventilation; local exhaust ventilation
Liberation during brush application of specialized surface coatings	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-methyl styrene 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-methyl styrene gets on the skin, promptly flush the contaminated skin with water. If alpha-methyl styrene 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 alpha-methyl styrene, 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 alpha-methyl styrene 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 alpha-methyl styrene 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. Liquid alpha-methyl styrene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

alpha-Methyl styrene 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.

REFERENCES

• Allied Chemical Company: *Material Safety Data Sheet - alpha-Methyl Styrene.*
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RESPIRATORY PROTECTION FOR ALPHA-METHYL STYRENE

Condition	Minimum Respiratory Protection* Required Above 100 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 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 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 Health Guideline for Mica

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: Muscovite (most important) is: $K_2Al_4(Al_2Si_6O_{20})(OH)_4$ (typical)
- Synonyms: Muscovite; amber mica; roscoelite; lepidolite; phlogopite; biotite; zinnwaldite; fluorophlogopite
- Appearance and odor: Colorless, odorless flakes or sheets containing less than 1% quartz (free crystalline silica).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for mica is 20 million particles of mica per cubic foot of air (mppcf) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Mica can affect the body if it is inhaled.

- **Effects of overexposure**

Exposure to mica dust over a period of years may cause scarring of the lungs. The symptoms which may occur with this condition are cough, shortness of breath, weakness, and weight loss.

- **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 mica.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to mica 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.

—14" x 17" chest roentgenogram: Mica causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Mica causes pneumoconiosis. 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.

- **Summary of toxicology**

Mica dust causes pneumoconiosis. In a study of 57 workers exposed to mica dust, 5 of the 6 workers exposed more than 10 years to concentrations in excess of 25 mppcf had pneumoconiosis. The most characteristic finding by chest x-ray was fine granulation of uneven density; there was a tendency to a coalescence of shadows in some cases. The symptoms most frequently reported were chronic cough and dyspnea; complaints of weakness and weight loss were less frequent.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Formula weight (muscovite): 797
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.6— 3.2
4. Vapor density (air = 1 at boiling point of mica): Not applicable
5. Melting point: Not applicable
6. Vapor pressure at 20 C (68 F): Essentially zero

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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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: None
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Mica 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**

At the time of publication of this guideline, no measurement method for mica 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 mica may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from open and underground mining operations	General dilution ventilation; local exhaust ventilation; dust collection; process enclosure; personal protective equipment; wet drilling
Use in manufacture of electrical insulation for low thermal conductivity and high dielectric strength	General dilution ventilation; local exhaust ventilation; dust collection; wet methods; personal protective equipment
Use in manufacture of asphalt shingles and roll roofing	General dilution ventilation; local exhaust ventilation; dust collection; process enclosure; personal protective equipment
Use in manufacture of paint, wall paper, and bituminized cardboard	General dilution ventilation; local exhaust ventilation; dust collection; wet methods; personal protective equipment
Use in manufacture of molded rubber products; plastics; special greases; absorbent of well drilling muds	General dilution ventilation; local exhaust ventilation; dust collection; personal protective equipment
Use in fabrication of windows and diaphragms	Process enclosure

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 mica 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.

- **Breathing**

If a person breathes in large amounts of mica, 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 spills or releases until cleanup has been completed.

• If mica is spilled or released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of spill or release.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a sanitary landfill.

• Waste disposal method:

Mica may be disposed of in a sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Mica," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• Schwartz, L., Tulipan, L., and Birmingham, D.: *Occupational Diseases of the Skin* (3rd. ed. rev.), Lea and Febiger, Philadelphia, 1957.

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RESPIRATORY PROTECTION FOR MICA

Condition	Minimum Respiratory Protection* Required Above 20 mppcf
Particulate Concentration	
100 mppcf or less	Any dust respirator.
200 mppcf or less	Any dust 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.
1000 mppcf 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.
10,000 mppcf 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 10,000 mppcf 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 Molybdenum and Insoluble Molybdenum

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 molybdenum and insoluble molybdenum compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Metallic molybdenum

- Formula: Mo
- Synonyms: None
- Appearance: Silvery white metal or gray-black powder.

Molybdenum disulfide

- Formula: MoS_2
- Synonyms: Molybdenite
- Appearance and odor: Shiny gray, odorless plates.

Lead molybdate

- Formula: $PbMoO_4$
- Synonyms: Sulfenite
- Appearance and odor: Colorless to pale yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for molybdenum and insoluble molybdenum compounds is 15 milligrams of molybdenum and insoluble molybdenum compounds 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 molybdenum and insoluble molybdenum compounds a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Molybdenum and insoluble molybdenum compounds can affect the body if they are inhaled or if they come in contact with the eyes. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Molybdenum trioxide has caused irritation of the eyes, nose, and throat, weight loss, and digestive disturbances 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 molybdenum and insoluble molybdenum compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to molybdenum and insoluble molybdenum compounds 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 molybdenum and insoluble molybdenum compounds exposure.

—Kidney disease: Fume from arcing molybdenum metal 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.

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 respiratory disease: Fume from arcing molybdenum metal causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of insoluble molybdenum compounds might cause exacerbation of symptoms due to their irritant properties.

—Liver disease: Fume from arcing molybdenum metal 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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

• **Summary of toxicology**

Molybdenum and its insoluble compounds, which include molybdenum disulfide, calcium molybdate, and many of the oxides and halides, have a low toxicity; however, molybdenum trioxide irritates the eyes and mucous membranes. Guinea pigs repeatedly exposed to molybdenum trioxide dust at a concentration of 200 mg molybdenum/m^3 for 1 hour daily developed nasal irritation, diarrhea, weight loss, and incoordination. In guinea pigs exposed to fume from arcing molybdenum metal, there were some deaths at 190 mg/m^3 but minimal effects at 53 mg/m^3; autopsy revealed bronchial and alveolar irritation with moderate fatty changes in the liver and kidneys. Animals receiving daily oral doses of up to 500 mg molybdenum per day in the form of molybdenum trioxide or calcium molybdate showed anorexia, listlessness, and weight loss. The metabolism of molybdenum is closely associated with that of copper; molybdenum toxicity to animals can be alleviated by the administration of copper. While molybdenum is essential to the action of certain enzymes, higher molybdenum levels may inhibit the action of these enzymes. High intake of molybdenum in rats resulted in a substantial reduction in activity of sulfide oxidase in the liver. The reduced activity of this enzyme leads to accumulation of sulfide in the tissues and subsequent formation of highly undissociated copper sulfide, thus removing copper from metabolic activity. This is a probable explanation for the induction of copper deficiency by molybdate. High dietary intake of molybdenum has been reported to be associated with a gout-like disease and high blood uric acid.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Metallic molybdenum**

1. Molecular weight: 95.94
2. Boiling point (760 mm Hg): 5,560 C (10,040 F)
3. Specific gravity (water = 1): 10.22
4. Vapor density (air = 1 at boiling point of metallic molybdenum): Not applicable
5. Melting point: 2,610 C (4,730 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—Molybdenum disulfide**

1. Molecular weight: 160.1
2. Boiling point (760 mm Hg): Oxidizes above 315 C (599 F)
3. Specific gravity (water = 1): 4.7
4. Vapor density (air = 1 at boiling point of molybdenum disulfide): Not applicable
5. Melting point: 1370 C (2498 F) (oxidizes above 315 C (599 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—Lead Molybdate**

1. Molecular weight: 367.1
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 6.8
4. Vapor density (air = 1 at boiling point of lead molybdate): Not applicable
5. Melting point: 1066 C (1950 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.000012
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of finely divided molybdenite with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as molybdenum oxide fume, sulfur dioxide gas, and carbon monoxide) may be released when insoluble molybdenum compounds decompose.
4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature: Molybdenum: 360 C (680 F) (layer); 720 C (1328 F) (cloud); Molybdenite: 290 C (554 F) (layer); 570 C (1058 F) (cloud)
3. Minimum explosive concentration: Data not available
4. Extinguishant: Molybdenum and molybdenum disulfide: Dry sand, dry dolomite, dry graphite

• **Warning properties**

None of the insoluble compounds of molybdenum are known to be significant eye irritants.

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 molybdenum and insoluble molybdenum compounds on a filter, followed by chemical treatment, and atomic absorption spectrophotometric analysis. An analytical method for molybdenum and insoluble molybdenum 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.

SANITATION

• Eating and smoking should not be permitted in areas where solids containing molybdenum and insoluble molybdenum compounds are handled, processed, or stored.

• Employees who handle solids or liquids containing insoluble molybdenum compounds 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 molybdenum and insoluble molybdenum compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining and processing of ore; from grinding and other abrasive treatment of metal or alloys for use in electrical contacts, spark plugs, x-ray tubes, grids for radio tubes, missle and aircraft parts, and iron/steel alloys	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as lubricants in greases, oil dispersions, resin-bonded films, and dry powders; as catalysts in petroleum refining and chemical processing	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in pigment mixture for labelling glass bottles, for printing inks, for paints, and for plastics; as reagents in analytical chemistry laboratories	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in powder as chemical intermediates; use in molybdic acid; use as alloying agents in production of iron/steel	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as catalysts in organic synthesis in medicinals, in decorative and protective coatings for metal, and as feed additives	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during temperature application as protective coatings for electrical resistors and engine parts, and as catalysts	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chemical intermediates and plating agents for mirrors; use in metal brazing and in manufacture of cutting tools	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

Liberation during use as solid lubricants	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation as catalysts in manufacture of propylene oxide	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in chemical laboratory	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.

• **Breathing**

If a person breathes in large amounts of molybdenum and insoluble molybdenum 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 molybdenum and insoluble molybdenum compounds 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 molybdenum and insoluble molybdenum 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 for reclamation, or for disposal in a secured sanitary landfill. Liquid containing insoluble molybdenum compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Molybdenum and insoluble molybdenum compounds may be disposed of in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Molybdenum as Mo," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR MOLYBDENUM AND INSOLUBLE MOLYBDENUM COMPOUNDS (AS MOLYBDENUM)

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Dust or Mist 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.
Dust, Mist, or Fume Concentration	
150 mg/m³ or less	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.
7,500 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 7,500 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 Health Guideline for Soluble Molybdenum Compounds (as Molybdenum)

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 molybdenum compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION— Molybdenum trioxide

- Formula: MoO_3
- Synonyms: Molybdenum anhydride; molybdic oxide
- Appearance and odor: Yellow to white, odorless solid.

SUBSTANCE IDENTIFICATION— Ammonium molybdate

- Formula: $(NH_4)_2MoO_4$
- Synonyms: 85% molybdic acid
- Appearance and odor: Yellow to white, odorless solid.

SUBSTANCE IDENTIFICATION— Ammonium paramolybdate

- Formula: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$
- Synonyms: None
- Appearance and odor: Yellow to white, odorless solid.

SUBSTANCE IDENTIFICATION— Calcium molybdate

- Formula: $CaMoO_4$
- Synonyms: None
- Appearance and odor: Yellow to white, odorless solid.

SUBSTANCE IDENTIFICATION— Sodium molybdate, dihydrate

- Formula: $Na_2MoO_4\cdot 2H_2O$
- Synonyms: Sodium molybdate
- Appearance: White crystalline powder.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble molybdenum compounds is 5 milligrams of soluble molybdenum compounds (as molybdenum) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble molybdenum compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They might also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Soluble molybdenum compounds have caused loss of appetite, incoordination, and irritation of eyes, nose, and throat, difficulty in breathing, anemia, and colic in animals.

2. Long-term Exposure: Animal data suggest that repeated exposure to soluble molybdenum compounds might be associated with gout.

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 molybdenum compounds.

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 molybdenum compounds at potentially hazardous levels:

1. Initial Medical Screening: Routine medical histories and physical examinations are not considered necessary. However, the employer should screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble molybdenum compounds exposure. Only those giving a positive history of these conditions should be referred for further medical examinations.

—Kidney disease: Although soluble molybdenum compounds are not known as kidney toxins 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 soluble molybdenum compounds might cause exacerbation of symptoms due to their irritant properties.

—Blood disease: Soluble molybdenum compounds cause anemia in animals. Persons with pre-existing blood disorders may be more susceptible to the effects of these agents.

—Gout: Soluble molybdenum compounds may cause gout. Persons with pre-existing conditions may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: Routine periodic examinations are not considered necessary. However, anyone developing the above listed conditions should be referred for further medical examination.

• **Summary of toxicology**

Soluble molybdenum compounds have a low toxicity but may cause anemia and deformities of the forelegs when fed to rabbits in high doses. In rats, the approximate oral LD50 for daily repeated doses of ammonium molybdate was 333 mg molybdenum/g/day; sodium molybdate was fatal to rabbits within a few weeks at a dietary level of 0.1%. In rats and guinea pigs, oral doses of 1.2 g/kg ammonium molybdate caused anorexia, colic, trembling, incoordination, and dyspnea; anemia and deformity of the forelegs occurred in rabbits. Exposure of mice for 1 hour to a high concentration of the dust of ammonium molybdate caused a transitory irritation of mucous membranes. While molybdenum is essential to the action of certain enzymes, higher molybdenum levels may inhibit the action of other enzymes. High intake of molybdenum in rats resulted in a substantial reduction in activity of sulfide oxidase in the liver. The reduced activity of this enzyme leads to accumulation of sulfide in the tissues and subsequent formation of highly undissociated copper sulfide, thus removing copper from metabolic activity. This is a probable explanation for the induction of copper deficiency by molybdate. There have been no reports of systemic effects from industrial exposure. A study from the Ankavan Province of Russia, where dietary molybdenum intake ranges from 10 to 15 mg per day due to high natural levels, has shown elevated blood xanthine oxidase activity and increased uric acid concentrations in blood of residents compared with controls living in an area with lower molybdenum exposure. A high percentage (31%) of the population examined from the Ankavan Province were diagnosed as having a gout-like disease.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Molybdic trioxide**

1. Molecular weight: 144
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 4.7
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: 795 C (1463 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.5
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Ammonium molybdate**

1. Molecular weight: 196
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.3
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Soluble, decomposes
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Ammonium paramolybdate**

1. Molecular weight: 1238
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 2.5
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 43
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Calcium molybdate**

1. Molecular weight: 200
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 4.35
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: 695 C (1283 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.01
8. Evaporation rate (butyl acetate = 1): Not applica-

ble

- **Physical data—Sodium molybdate, dihydrate**

1. Molecular weight: 241.95
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 3.28
4. Vapor density (air = 1 at boiling point of soluble molybdenum compounds): Not applicable
5. Melting point: Loses its water at 100 C (212 F)
6. Vapor pressure at 20 C (68 F): Data not available
7. Solubility in water, g/100 g water at 0 C (32 F): 56.2
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Ammonium molybdate and ammonium paramolybdate decompose above 360 C (680 F). Other are stable.
2. Incompatibilities: Contact with alkali metals such as sodium and potassium or with molten magnesium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as ammonia and carbon monoxide) may be released when some soluble molybdenum compounds decompose.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

According to Patty, "exposure to molybdenum oxide is irritating to eyes . . .," but he gives no quantitative information concerning the concentrations necessary. Examples of molybdenum compounds which cause eye irritation are: compounds containing nitrate, acetate, chloride, trioxide, and molybdate.

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 soluble molybdenum compounds on a filter, followed by leaching-off of analyte with hot water and atomic absorption spectrophotometric analysis. An analytical method for soluble molybdenum 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 soluble molybdenum compounds or liquids containing soluble molybdenum compounds.
- Non-impervious clothing which becomes contaminated with soluble molybdenum compounds should be removed promptly and not reworn until the soluble molybdenum compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble molybdenum compounds or liquids containing soluble molybdenum compounds may contact the eyes.

SANITATION

- Skin that becomes contaminated with soluble molybdenum compounds should be promptly washed or showered with soap or mild detergent and water to remove any soluble molybdenum compounds.
- Eating and smoking should not be permitted in areas where soluble molybdenum compounds are handled, processed, or stored.
- Employees who handle soluble molybdenum compounds or liquids containing soluble molybdenum compounds 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 soluble molybdenum compounds

may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during rolling of hot billets in processing molybdenum steel; for use as electrodes; during welding operations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chemical reagent for laboratory analyses; in petroleum refining and chemical processing; as an intermediate in the manufacture of corrosion inhibitors; use as coloring agents for enamels and ceramic glazes; agricultural chemicals	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in electroplating process; use in formulation of corrosion inhibitors for aqueous systems; pigments for paints, lacquers, and coloring animal fibers and hair	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in enamel processes for adherence of vitreous coatings to ceramics and metal; use in leather and skin tanning	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as chlorination catalysts; in fire-retardant resins; as a brazing flux and as an intermediate for organo-metallic compounds; use in photography; ion exchange processes and formulation of plastics and adhesives; as a catalyst in desulfurization of gasoline; use as a reagent for determination of phosphorus and lead	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 soluble molybdenum compounds or liquids containing soluble molybdenum compounds 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 soluble molybdenum compounds or liquids containing soluble molybdenum compounds get on the skin, flush the contaminated skin with water. If soluble molybdenum compounds or liquids containing soluble molybdenum compounds penetrate through the clothing, remove the clothing and flush the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of soluble molybdenum 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 molybdenum compounds or liquids containing soluble molybdenum 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 molybdenum compounds or liquids containing soluble molybdenum 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 molybdenum compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:
Soluble molybdenum compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Molybdenum as Mo," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR SOLUBLE MOLYBDENUM COMPOUNDS (AS MOLYBDENUM)

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
25 mg/m³ or less	Any dust or mist respirator**.
50 mg/m³ or less	Any dust and mist respirator, except single-use or quarter mask respirators**. Any high efficiency particulate filter respirator**.
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.
5000 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
10,000 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 10,000 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. Any escape self-contained breathing apparatus.

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

**In those cases where eye irritation occurs, full facepiece respirators are recommended. Examples of molybdenum compounds which cause eye irritation are: compounds containing nitrate, acetate, chloride, trioxide, and molybdate.

Occupational Health Guideline for Monomethyl Aniline

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: $C_6H_5NH(CH_3)$
- Synonyms: N-Methyl aniline; MA; methyl aniline
- Appearance and odor: Yellow to light brown liquid with a weak, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for monomethyl aniline is 2 parts of monomethyl aniline per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 9 milligrams of monomethyl aniline per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for monomethyl aniline a Threshold Limit Value of 0.5 ppm with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Monomethyl aniline 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**

1. Short-term Exposure: Monomethyl aniline may cause a bluish discoloration of the skin. Headache, dizziness, weakness, drowsiness, and unconsciousness may also 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 monomethyl aniline.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to monomethyl aniline 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, and blood should be stressed.

—A complete blood count: Monomethyl aniline has been shown to cause methemoglobinemia and anemia in animals. 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 and a methemoglobin determination.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Monomethyl aniline vapor causes anoxia due to the formation of methemoglobin. Animal fatalities occurred from daily exposures to 7.6 ppm; signs of intoxication included prostration, labored breathing, and cyanosis; methemoglobinemia developed promptly in rabbits and cats; the rabbits also exhibited mild anemia and bone marrow hyperplasia. Autopsy of animals that died revealed pulmonary involvement ranging from edema to interstitial pneumonia, as well as occasional centrilobular hepatic necrosis and moderate kidney damage. The liquid readily caused poisoning in animals by absorption through the skin. No effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 107.2

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

2. Boiling point (760 mm Hg): 195.6 C (384 F)
3. Specific gravity (water = 1): 0.99
4. Vapor density (air = 1 at boiling point of monomethyl aniline): 3.70
5. Melting point: −80 C (-112 F) (approximately)
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): Moderate
8. Evaporation rate (butyl acetate = 1): Less than 1

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of liquid monomethyl aniline with strong acids will cause violent spattering. 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 in a fire involving monomethyl aniline.
4. Special precautions: Liquid monomethyl aniline will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 79.4 C (175 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, alcohol foam

• **Warning properties**

1. Odor Threshold: Cyanamid's *Chemical Safety Data Sheet* states that monomethyl aniline has a "moderate aniline-type odor," but no quantitative information is available concerning the odor threshold.
2. Eye Irritation Level: Monomethyl aniline vapor is not a known eye irritant.
3. Evaluation of Warning Properties: Since no information is available relating warning properties of monomethyl aniline to air concentrations, the substance is considered to have 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 monomethyl aniline in a bubbler filled with sulfuric acid, followed by treatment with sodium hydroxide, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure monomethyl aniline may be used. An analytical method for monomethyl aniline 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 respir tory protection program should be instituted whic includes regular training, maintenance, inspectio cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required use impervious clothing, gloves, face shields (eight-in minimum), and other appropriate protective clothi necessary to prevent skin contact with liquid mo methyl aniline, where skin contact may occur.

• Clothing contaminated with monomethyl anil should be placed in closed containers for storage unt can be discarded or until provision is made for removal of monomethyl aniline from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the monomethyl aniline, the person performing the operation should be informed of monomethyl aniline's hazardous properties.

• Non-impervious clothing which becomes contaminated with monomethyl aniline should be removed immediately and not reworn until the monomethyl aniline is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid monomethyl aniline may contact the eyes.

SANITATION

• Skin that becomes contaminated with liquid monomethyl aniline should be immediately washed or showered with soap or mild detergent and water to remove any monomethyl aniline.

• Eating and smoking should not be permitted in areas where liquid monomethyl aniline is handled, processed, or stored.

• Employees who handle liquid monomethyl aniline 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 monomethyl aniline may occur and control methods which may be effective in each case:

Operation	Controls
Use during organic synthesis and in dye intermediates	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 monomethyl aniline 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 monomethyl aniline gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If monomethyl aniline soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention.

• **Breathing**

If a person breathes in large amounts of monomethyl aniline, 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 monomethyl aniline has 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 or leaks until cleanup has been completed.

• If monomethyl aniline 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.

• Waste disposal methods:

Monomethyl aniline 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.

REFERENCES

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RESPIRATORY PROTECTION FOR MONOMETHYL ANILINE

Condition	Minimum Respiratory Protection* Required Above 2 ppm
Vapor Concentration	
20 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
100 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 with a half facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 100 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 monomethyl aniline. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Morpholine

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_9ON
- Synonyms: Tetrahydro-1,4-oxazine; diethyleneimide oxide
- Appearance and odor: Colorless liquid with a weak, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for morpholine is 20 parts of morpholine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 70 milligrams of morpholine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Morpholine 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**

1. Short-term Exposure: Morpholine may cause irritation of the eyes, nose, throat, lungs, and skin.

2. Long-term Exposure: Repeated or prolonged overexposure to morpholine 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 morpholine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to morpholine 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 morpholine exposure.

—Chronic respiratory disease: Morpholine causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of morpholine might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Morpholine 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: Morpholine 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.

—Eye disease: Morpholine is an eye irritant and has caused corneal edema in workers. Persons with preexisting eye disorders may be more susceptible to the effects of this agent.

—Skin disease: Morpholine is a primary skin irritant and induces hypersensitive responses. Persons with preexisting 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**

Morpholine vapor is an irritant to the skin, eyes, mucous membranes, and the respiratory tract. Hypersensitivity is common. Repeated daily exposure of rats to 18,000 ppm was lethal to some animals; those dying during the third to fifth days of exposure revealed damage to lungs, liver, and kidneys. A human exposure

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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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to 12,000 ppm for 1-½ minutes in a laboratory produced nose irritation and cough; mouth pipetting of the liquid caused a severe sore throat and reddened mucous membranes. The liquid dropped in the eye of a rabbit caused moderate injury with ulceration of the conjunctiva and corneal clouding. Workers exposed for several hours to low vapor concentrations complained of foggy vision with rings around lights, the result of corneal edema which cleared within 3 to 4 hours after cessation of exposure. The liquid is a severe skin irritant and may produce contact dermatitis. In industry, some instances of skin and respiratory tract irritation have been observed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 87.1
  2. Boiling point (760 mm Hg): 128 C (263 F)
  3. Specific gravity (water = 1): 1.0
  4. Vapor density (air = 1 at boiling point of morpholine): 3.0
  5. Melting point: −4.8 C (23 F)
  6. Vapor pressure at 20 C (68 F): 7 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): Less than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact of liquid morpholine with strong acids will cause violent spattering. 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 in a fire involving morpholine.
  4. Special precautions: Liquid morpholine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 35 C (95 F) (closed cup)
  2. Autoignition temperature: 310 C (590 F)
  3. Flammable limits in air, % by volume: Lower: 1.8 (calculated); Upper: 11 (estimated)
  4. Extinguishant: Carbon dioxide, dry chemical, alcohol foam
- **Warning properties**
  1. Odor Threshold: Grant states that morpholine has a characteristic amine odor. No quantitative information is available concerning the odor threshold, however.
  2. Eye Irritation Level: Grant reports that lacrimation has been observed among experimental animals and among industrial workers who have been exposed to high vapor concentrations. "At low concentrations in air, morpholine has been listed with its N-ethyl and N-methyl derivatives among the amines which have been observed to cause transient edema of the cornea and temporary foggy vision with haloes around lights in workers exposed to the vapors for many hours, the symptoms usually coming on after work and clearing spontaneously by the next day."

  Patty also reports that morpholine irritates the mucous membranes.

  No quantitative information is available, however, concerning the threshold of eye irritation.

  3. Other Information: Both Patty and Grant note that morpholine is a respiratory tract irritant, but no quantitative information is available concerning the threshold of this irritation.

  4. Evaluation of Warning Properties: Since no quantitative information relating warning properties to air concentrations is available, morpholine is treated as a substance 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 morpholine in an adsorption tube containing silica gel, followed by desorption with sulfuric acid, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure morpholine may be used. An analytical method for morpholine 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 liquid morpholine or solutions containing greater than 25% morpholine by weight and to prevent repeated or prolonged skin contact with solutions containing 25% or less of morpholine by weight.
• Clothing contaminated with morpholine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of morpholine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the morpholine, the person performing the operation should be informed of morpholine's hazardous properties.
• Where there is any possibility of exposure of an employee's body to liquid morpholine or solutions containing greater than 25% morpholine by weight, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
• Any clothing which becomes wet with liquid morpholine should be removed immediately and not reworn until the morpholine is removed from the clothing.
• Non-impervious clothing which becomes contaminated with morpholine should be removed promptly and not reworn until the morpholine 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 morpholine or solutions containing morpholine contacting the eyes.
• Where there is any possibility that employees' eyes may be exposed to liquid morpholine or solutions containing greater than 15% morpholine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with morpholine should be promptly washed or showered to remove any morpholine.
• Employees who handle liquid morpholine or solutions containing morpholine 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 morpholine may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of rubber chemicals for rubber accelerators, catalysts, plasticizers, curing agents, stabilizers of halogenated butyl rubber, and emulsifying agents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a corrosion inhibitor in steam boiler systems, petroleum refining, sterilization autoclaves, and in natural gas processing; use in manufacture of optical brightening agents in bleaches and detergents	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in compounding of waxes and polishes for commercial use as automobile waxes, rubless waxes and polishes, and water-resistant polishes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate for textile industry as lubricants, sizing emulsifiers, and softening agents; in pharmaceutical industry as bactericides, analgesics, anesthetics, anti-spasmotics, and anti-malarials; in chemical industry for alkyl morpholines, emulsifying agents, surface-active agents, cosmetics, and soap emulsifiers; in agriculture for protective coatings for fresh fruits and vegetables, pesticide emulsifiers, insecticides, fumigants, and herbicides	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for dyes, waxes, resins, and casein	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 morpholine or solutions containing morpholine 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 morpholine or solutions containing morpholine get on the skin, immediately flush the contaminated skin with water. If liquid morpholine or solutions containing morpholine 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 morpholine, 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 morpholine has 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 or leaks until cleanup has been completed.

• If morpholine 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. Morpholine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Morpholine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on morpholine, look up morpholine 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.

REFERENCES

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RESPIRATORY PROTECTION FOR MORPHOLINE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Vapor Concentration	
1000 ppm or less	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.

Occupational Health Guideline for Naphtha (Coal Tar)

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_7H_8 – C_8H_{10} (approximately)
- Synonyms: Naphtha, 49 degrees Be-coal tar type; crude solvent coal tar naphtha; high-solvent coal tar naphtha
- Appearance and odor: Reddish-brown, mobile liquid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for coal tar naphtha is 100 parts of coal tar naphtha per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 400 milligrams of coal tar naphtha per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Coal tar naphtha can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to coal tar naphtha can cause lightheadedness, drowsiness, and unconsciousness. It also may cause mild irritation of the eyes, nose, and skin.

2. Long-term Exposure: Prolonged overexposure to coal tar naphtha 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 coal tar naphtha.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to coal tar naphtha 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 coal tar naphtha exposure.

—Skin disease: Coal tar naphtha 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 coal tar naphtha 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 coal tar naphtha 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 coal tar naphtha 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**

Coal tar naphtha vapor is narcotic. Rats survived continuous exposure at 3200 ppm for two months; at 1800 ppm some animals showed damage to the liver and kidneys; above 1000 ppm there was evidence of narcotic action. Rats exposed at 567 ppm and 312 ppm for 18 to 20 hours a day for 7 days had some reduction in blood leukocytes, possibly the result of the presence of benzene. There are few if any well documented reports of industrial injury resulting from the inhalation of

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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naphtha. However, exposure to high concentrations might be expected to cause lightheadedness, drowsiness, and possibly irritation of the eyes, nose, and throat. Repeated or prolonged contact with the liquid may result in drying and cracking skin due to defatting action. Coal tar (naphtha) is a non-uniform mixture of aromatic hydrocarbons and may contain benzene.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 110 (approximately)
2. Boiling point (760 mm Hg): 110 to 190 C (230 to 374 F)
3. Specific gravity (water = 1): 0.97
4. Vapor density (air = 1 at boiling point of coal tar naphtha): 3 (approximately)
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Less than 5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Greater 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 carbon monoxide) may be released in a fire involving coal tar naphtha.
4. Special precautions: Coal tar naphtha will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 38 to 43 C (100 to 109 F) (closed cup)
2. Autoignition temperature: 482 to 510 C (900 to 950 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Since the odor thresholds of the main constituents of coal tar naphtha are below their permissible exposure limits, the odor threshold of coal tar naphtha is assumed to be below the permissible exposure limit.
2. Eye Irritation Level: According to Grant, Gafafer states that the naphthas cause conjunctival irritation. Two of the main constituents of coal tar naphtha, xylene and toluene, cause noticeable eye irritation at concentrations of 200 and 300 ppm, respectively.
3. Evaluation of Warning Properties: Since the odor threshold of the main constituents of coal tar naphtha are well below their permissible exposure limits, coal tar naphtha 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 coal tar naphtha 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 coal tar naphtha may be used. An analytical method for coal tar naphtha 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).
026).

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 coal tar naphtha.
- Clothing wet with liquid coal tar naphtha should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

coal tar naphtha from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the coal tar naphtha, the person performing the operation should be informed of coal tar naphtha's hazardous properties.

- Non-impervious clothing which becomes wet with liquid coal tar naphtha should be removed promptly and not reworn until the coal tar naphtha is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid coal tar naphtha may contact the eyes.

SANITATION

- Skin that becomes wet with liquid coal tar naphtha should be promptly washed or showered with soap or mild detergent and water to remove any coal tar naphtha.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to coal tar naphtha may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of coal-tar paints	Process enclosure; general dilution ventilation; personal protective equipment
Use in preparation of coumarone and indene	General dilution ventilation; personal protective equipment
Use as a solvent in rubber industry in manufacture of water-proof cloth, shoe adhesives, and rubber tires	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent, diluent, or thinner in paint, varnish, and lacquer industries	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in formulations of nitrocellulose and ethylcellulose	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent for polymerized styrol, short-oil phenolic varnishes, urea, resins, melamine, and other synthetic resins; use as a solvent for pesticides as DDT and Gammexane	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 coal tar naphtha gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If coal tar naphtha gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If coal tar naphtha soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of coal tar naphtha, 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 coal tar naphtha 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 coal tar naphtha 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. Coal tar naphtha should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Coal tar naphtha 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 NAPHTHA (COAL TAR)

Condition	Minimum Respiratory Protection* Required Above 100 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 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.
10,000 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 10,000 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 Naphthalene

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: $C_{10}H_8$
- Synonyms: White tar; naphthalin
- Appearance and odor: Colorless to brown solid with the odor of mothballs.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for naphthalene is 10 parts of naphthalene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 50 milligrams of naphthalene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Naphthalene 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 or ingestion of naphthalene may cause abdominal cramps, nausea, vomiting, diarrhea, headache, tiredness, confusion, painful urination, and bloody or dark urine. Swallowing large amounts may cause convulsions or coma. Inhalation, ingestion, and possibly skin absorption of naphthalene may cause destruction of red blood cells with anemia, fever, yellow jaundice, bloody urine, kidney and liver damage. Naphthalene, on contact with the eyes, has produced irritation. Naphthalene, on contact with the skin, has produced skin irritation.

2. Long-term Exposure: Repeated skin exposure to naphthalene may cause an allergic rash. Repeated exposure may cause cataracts.

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 naphthalene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to naphthalene 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 deficiency of glucose-6-phosphate dehydrogenase in erythrocytes may be at increased risk from exposure. Examination of the eyes, blood, liver and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Naphthalene has been shown to cause red blood cell hemolysis. A complete blood count should be performed, including a red cell count, a white cell count, and a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Urinalysis: Since kidney damage may also occur from exposure to naphthalene, a urinalysis should be performed, including 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**

Naphthalene vapor causes hemolysis and eye irritation; it may cause cataracts. Severe intoxication from ingestion of the solid results in characteristic manifestations of marked intravascular hemolysis and its consequences, including potentially fatal hyperkalemia. Initial symptoms include eye irritation, headache, confu-

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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sion, excitement, malaise, profuse sweating, nausea, vomiting, abdominal pain, and irritation of the bladder; there may be progression to jaundice, hematuria, hemoglobinuria, renal tubular blockage, and acute renal shutdown. Hematologic features include red cell fragmentation, icterus, severe anemia with nucleated red cells, leukocytosis, and dramatic decreases in hemoglobin, hematocrit, and red cell count; sometimes there is formation of Heinz bodies and methemoglobin. Individuals with a deficiency of glucose-6-phosphate dehydrogenase in erythrocytes may be more susceptible to hemolysis by naphthalene. Cataracts and ocular irritation have been produced experimentally in animals and have been described in humans; of 21 workers exposed to high concentrations of fume or vapor for 5 years, 8 had peripheral lens opacities; in other studies no abnormalities of the eyes have been detected in workers exposed to naphthalene for several years. The vapor causes eye irritation at 15 ppm; eye contact with the solid may result in conjunctivitis, superficial injury to the cornea, chorioretinitis, scotoma, and diminished visual acuity. Naphthalene on the skin may cause hypersensitivity dermatitis; chronic dermatitis is rare.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 128.2
2. Boiling point (760 mm Hg): 218 C (424 F)
3. Specific gravity (water = 1): 1.14
4. Vapor density (air = 1 at boiling point of naphthalene): 4.4
5. Melting point: 74 – 80 C (165 – 176 F)
6. Vapor pressure at 20 C (68 F): 0.05 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.003
8. Evaporation rate (butyl acetate = 1): Much less than 1

- **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 dense acrid smoke and carbon monoxide) may be released in a fire involving naphthalene.
4. Special precautions: Melted naphthalene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 79 C (174 F) (closed cup)
2. Autoignition temperature: 526 C (979 F)
3. Flammable limits in air, % by volume: Lower: 0.9; Upper: 5.9
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* reports that the odor threshold of naphthalene is "at least as low as 0.3 ppm."
2. Eye Irritation Level: The *Hygienic Guide* states that "naphthalene vapor is reported to cause eye irritation at 15 ppm or above in air."
3. Evaluation of Warning Properties: Through its odor and irritant effects, naphthalene can be detected at or below the permissible exposure limit. Naphthalene, therefore, 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 naphthalene may be used. An analytical method for naphthalene 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 repeated or prolonged skin contact with naphthalene or liquids containing naphthalene.
• If employees' clothing may have become contaminated with solid naphthalene, employees should change into uncontaminated clothing before leaving the work premises.
• Clothing contaminated with naphthalene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of naphthalene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the naphthalene, the person performing the operation should be informed of naphthalene's hazardous properties.
• Non-impervious clothing which becomes contaminated with naphthalene should be removed promptly and not reworn until the naphthalene is removed from the clothing.
• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid naphthalene or liquids containing naphthalene may contact the eyes.

SANITATION

• Skin that becomes contaminated with naphthalene should be promptly washed or showered with soap or mild detergent and water to remove any naphthalene.
• Eating and smoking should not be permitted in areas where solid naphthalene is handled, processed, or stored.
• Employees who handle naphthalene or liquids containing naphthalene 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 naphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of insecticide and moth repellant as flakes, powder, balls, or cakes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a fumigant for moth repellant and insecticide	General dilution ventilation; personal protective equipment
Use in manufacture of chemical intermediates for production of pharmaceuticals, resins, dyes, plasticizers, solvents, coatings, insecticides, pigments, rubber chemicals, tanning agents, surfactants, waxes, cable coatings, textile spinning lubricants, rodenticides, and in storage batteries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of naphthalene	Local exhaust ventilation; process enclosure; 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 naphthalene or liquids containing naphthalene 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 molten naphthalene gets on the skin, immediately flush the skin with large amounts of water. Get medical attention immediately. If naphthalene or liquids containing naphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If naphthalene or liquids containing naphthalene 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 naphthalene, move the exposed person to fresh air at once.

• **Swallowing**

When naphthalene 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 some-

one 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 naphthalene 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.

• Waste disposal methods:

Naphthalene may be disposed of:

1. By making packages of naphthalene in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving naphthalene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

ADDITIONAL INFORMATION

To find additional information on naphthalene, look up naphthalene 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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RESPIRATORY PROTECTION FOR NAPHTHALENE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Particulate and Vapor Concentration	
500 ppm or less	A chemical cartridge respirator with a full facepiece, 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 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 and particulates. Any escape self-contained breathing apparatus.

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

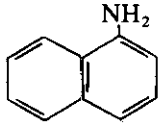
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR alpha-NAPHTHYLAMINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about alpha-naphthylamine 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:** $C_{10}H_9N$
- **Structure:**



- **Synonyms:** 1-Naphthylamine; 1-aminonaphthalene; naphthalidam; naphthalidine
- **Identifiers:** CAS 134-32-7; RTECS QM1400000; DOT 2077, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Colorless to yellow crystals which darken in air to a reddish purple color with a weak ammonia-like odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 143.20
2. Boiling point (at 760 mmHg): 301°C (573.8°F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of alpha-naphthylamine): 4.93
5. Melting point: 50°C (122°F)
6. Vapor pressure at 104°C (219°F): 1 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): 0.17

- **Reactivity**

1. Incompatibilities: alpha-naphthylamine oxidizes in air
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving alpha-naphthylamine.

- **Flammability**

1. Flash point: 157°C (315°F) (closed cup)
2. Extinguishant: Water, dry chemical, carbon dioxide, or alcohol foam
3. 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 alpha-naphthylamine; however, the OSHA standard requires implementation of stringent controls wherever alpha-naphthylamine or solid or liquid mixtures containing at least 0.1% by weight or volume of alpha-naphthylamine are manufactured, processed, repackaged, released, handled, or stored (see "General Control Procedure"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1004, alpha-Naphthylamine. 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 alpha-naphthylamine.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

alpha-Naphthylamine may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* In mice and dogs, chronic oral administration or subcutaneous injection of alpha-naphthylamine produced inconclusive evidence of liver, bladder, lung, or lymphatic cancer; however, beta-naphthylamine, which is a contaminant in commercial grade alpha-naphthylamine, is a recognized animal carcinogen. In addition, certain metabolites of alpha-naphthylamine have been shown to be carcinogenic in animals (e.g., N-(1-naphthyl)-hydroxylamine induces bladder cancer in mice, and 1-nitrosonaphthalene induces tumors in rats).

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2. *Effects on humans:* Long-term exposure of workers to commercial alpha-naphthylamine (which contains 4%-10% beta-naphthylamine) has been associated with an increased incidence of bladder cancer.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to alpha-naphthylamine can cause mild skin and eye irritation.

2. *Long-term (chronic):* Exposure to alpha-naphthylamine can cause headache, dizziness, a feeling of euphoria, weakness, impaired muscular coordination (ataxia), bluish discoloration of skin and mucous membranes (due to methemoglobinemia), breathing difficulty (dyspnea), blood in the urine, and painful, difficult, or frequent 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 alpha-naphthylamine, 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, lymphatic system, 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 alpha-naphthylamine. 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 alpha-naphthylamine. 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, lymphatic system, and urinary tract 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 alpha-naphthylamine 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: Bladder cancer.

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting alpha-naphthylamine dust with glass-fiber filters and silica gel tubes followed by elution with acetic acid in 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure alpha-naphthylamine may also be used if available. A detailed sampling and analytical method for alpha-naphthylamine may be found in the *NIOSH Manual of Analytical Methods* (method number 264).

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 alpha-naphthylamine 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 alpha-naphthylamine 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 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 alpha-naphthylamine 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 alpha-naphthylamine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of alpha-naphthylamine'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 alpha-naphthylamine 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 1910.1004:

Areas where alpha-naphthylamine 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 alpha-naphthylamine, 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 alpha-naphthylamine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of alpha-naphthylamine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where alpha-naphthylamine 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 alpha-naphthylamine 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 alpha-naphthylamine from the materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to alpha-naphthylamine 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 alpha-naphthylamine

Operations	Controls
During use in the manufacture of dyes, herbicides, and rubber antioxidants; during use in research facilities and laboratories	Process enclosure, restricted access, local exhaust ventilation where appropriate, 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 comes in contact with alpha-naphthylamine, 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 alpha-naphthylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If alpha-naphthylamine 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 alpha-naphthylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If alpha-naphthylamine gets on the skin, wash it immediately with soap and water. If alpha-naphthylamine 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.

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

If alpha-naphthylamine 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, alpha-naphthylamine may be collected and placed in an appropriate container.
4. alpha-Naphthylamine solid or liquid 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 alpha-naphthylamine 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.
5. For small quantities of liquids containing alpha-naphthylamine, absorb on paper towels and place in an appropriate container.
6. Large quantities of liquids containing alpha-naphthylamine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.

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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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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).

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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 alpha-naphthylamine

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.

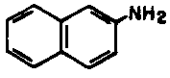
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR beta-NAPHTHYLAMINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about beta-naphthylamine 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:** $C_{10}H_9N$
- **Structure:**



- **Synonyms:** 2-Naphthylamine, 2-aminonaphthalene, 2-naphthalamine, 2-naphthalenamine
- **Identifiers:** CAS 91-59-8; RTECS QM2100000; DOT 1650, label required: "Poison"
- **Appearance and odor:** Odorless, white to reddish, crystals which darken in air to a reddish-purple color

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 143.20
2. Boiling point (at 760 mmHg): 306°C (583°F)
3. Specific gravity (water = 1): 1.061
4. Vapor density (air = 1 at boiling point of beta-naphthylamine): 4.95
5. Melting point: 110.2°C (230.4°F)
6. Vapor pressure at 108°C (226.4°F): 1 mmHg
7. Soluble in water

- **Reactivity**

1. Incompatibilities: beta-Naphthylamine oxidizes slowly in the presence of air and light.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving beta-naphthylamine.

- **Flammability**

1. Extinguishant: Dry chemical, foam, carbon dioxide, water
2. Combustible solid, no NFPA flammability rating

- **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 beta-naphthylamine; however, the OSHA standard requires implementation of stringent controls wherever beta-naphthylamine or solid or liquid mixtures containing at least 0.1% by weight or volume of beta-naphthylamine are manufactured, processed, repackaged, packaged, released, handled, or stored (see "General Control Procedures"). Details of this standard can be found in the Code of Federal Regulations, 29 CFR 1910.1009, beta-Naphthylamine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated beta-naphthylamine as an A1 substance (confirmed human carcinogen). The ACGIH recommends that no exposure or contact by any route be permitted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on animals:* Chronic oral administration of beta-naphthylamine produced liver cancer in mice and bladder cancer in hamsters, dogs, and monkeys.
2. *Effects on humans:* Acute exposure to beta-naphthylamine dust or vapor has caused bladder inflammation with bleeding (hemorrhagic cystitis). Chronic exposure to beta-naphthylamine alone or to beta-naphthylamine as an impurity in other compounds has been associated with an increased incidence of 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

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to beta-naphthylamine can cause weakness, dizziness, feeling of euphoria, breathing difficulty (dyspnea), bluish discoloration of the skin and mucous membranes (due to methemoglobinemia), and irritation of the skin and eyes.
2. *Long-term (chronic):* Exposure to beta-naphthylamine can cause frequent, painful, or difficult urination or blood in the urine.

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 beta-naphthylamine, 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, lymphatic system, 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 beta-naphthylamine. 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 beta-naphthylamine. 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, lymphatic system, and urinary tract 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 beta-naphthylamine 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: Bladder cancer.

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting beta-naphthylamine dust with glass fiber filters and silica gel tubes followed by elution with acetic acid in 2-propanol and analysis by gas chromatography. Direct-reading devices calibrated to measure beta-naphthylamine may also be used if available. A detailed sampling and analytical method for beta-naphthylamine may be found in the *NIOSH Manual of Analytical Methods* (method number 264).

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 beta-naphthylamine 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 beta-naphthylamine 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 beta-naphthylamine 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 beta-naphthylamine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of beta-naphthylamine'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 beta-naphthylamine 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, 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 1910.1009:

Areas where beta-naphthylamine 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 are 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 beta-naphthylamine, 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.

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Table 2.—Respiratory protection for beta-naphthylamine

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 high-efficiency particulate filter
	Any appropriate escape-type self-contained breathing apparatus

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

Occupational Health Guideline for Nickel Carbonyl*

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: $Ni(CO)_4$
- Synonyms: None
- Appearance and odor: Colorless liquid with a musty odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nickel carbonyl is 0.001 part of nickel carbonyl per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.007 milligram of nickel carbonyl per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be retained, but has recommended that nickel carbonyl be regulated as an occupational carcinogen. The NIOSH Special Occupational Hazard Review for Nickel Carbonyl and the NIOSH Criteria Document for Inorganic Nickel should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nickel carbonyl 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: Depending on the severity of inhalation exposure, both initial and delayed symptoms may develop. Initial symptoms include dizziness, headache, shortness of breath, and vomiting. These symptoms generally disappear when the individual is removed from exposure. The delayed symptoms may develop 12 to 36 hours after exposure. These symptoms include chest pain, cough, rapid breathing, shortness of breath, a bluish discoloration of the skin, and increased temperature. Delirium and other signs of nervous system problems usually appear at this time. In some cases the two stages may merge. In severe cases death may occur.

2. Long-term Exposure: Repeated or prolonged exposure to nickel carbonyl has been associated with an increased incidence of cancer of the lungs and sinuses.

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 nickel carbonyl.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nickel carbonyl 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 and upper respiratory tract should be stressed.

—14" x 17" chest roentgenogram: Nickel carbonyl causes human lung damage and is a suspected lung carcinogen. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nickel carbonyl is a severe pulmonary irritant. Persons with decreased pulmonary function may be at increased risk from exposure.

—Sputum cytology: Nickel carbonyl is associated with an increase of lung cancer in humans.

—Urinalysis: Since kidney damage has been observed from exposure, a urinalysis should be performed to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Examination of the urine for nickel should be conducted on a monthly 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.

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2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception that a urinalysis should be conducted on a monthly basis.

• **Summary of toxicology**

Nickel carbonyl vapor is a severe pulmonary irritant and probably causes cancer of the paranasal sinuses and the lungs in animals and man. Initial symptoms of overexposure usually include frontal headache, vertigo, nausea, vomiting, and sometimes substernal and epigastric pain; generally these early effects disappear when the individual is removed to fresh air. There may be an asymptomatic interval between recovery from initial symptoms and the onset of delayed symptoms, which tend to develop 12 hours or more following exposure; constrictive pain in the chest is characteristic of the delayed onset of pulmonary effects, followed by cough, hyperpnea and cyanosis, leading to profound weakness; gastrointestinal symptoms may also occur. The temperature seldom rises above 101 F, and leukocytosis above 12,000 per mg/m^3 is infrequent. Physical signs compatible with pneumonitis or bronchopneumonia are elicited in the chest. Except for the pronounced weakness and hyperpnea, the physical findings and symptoms resemble those of a viral or influenzal pneumonia. Terminally, delirium and convulsions frequently occur; death has occurred from 3 to 13 days after exposure to nickel carbonyl. In subjects who recover from nickel carbonyl intoxication, convalescence is usually protracted (2 to 3 months) and is characterized by excessive fatigue on slight exertion. Exposure of rats to nickel carbonyl has caused pulmonary carcinomata; multiple intravenous injection of nickel carbonyl in rats has caused carcinomata and sarcomata in diverse organs, including the liver and kidneys. Several epidemiologic studies have shown an increased incidence of cancer of the paranasal sinuses and lungs among workers in nickel refineries and factories; suspicion of carcinogenicity has been focused primarily on nickel carbonyl vapor, although there are usually concurrent exposures to respirable particles of nickel, nickel subsulfide, and nickel oxide.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 170.7
2. Boiling point (760 mm Hg): 43 C (109 F)
3. Specific gravity (water = 1): 1.32
4. Vapor density (air = 1 at boiling point of nickel carbonyl): 5.89
5. Melting point: −25 C (−13 F)
6. Vapor pressure at 20 C (68 F): 321 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.018
8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Liquid nickel carbonyl may explode when heated above 60 C (140 F). In the presence of air, nickel carbonyl forms a deposit which becomes peroxidized. This tends to decompose and ignite.
2. Incompatibilities: Contact with nitric acid, chlorine, and other oxidizers may cause fires and explosions. The vapor of nickel carbonyl may promote the ignition of mixtures of combustible vapors (such as gasoline) and air.
3. Hazardous decomposition products: Toxic gases and vapors (such as nickel oxide fume and carbon monoxide) may be released in a fire involving nickel carbonyl.
4. Special precautions: Liquid nickel carbonyl will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Lower than −20 C (−4 F) (closed cup)
2. Autoignition temperature: May ignite spontaneously
3. Flammable limits in air, % by volume: Lower: 2; Upper: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical

• **Warning properties**

1. Odor Threshold: Patty states that the odor of nickel carbonyl is detectable at between 1 and 3 ppm.
2. Eye Irritation Level: According to the AIHA *Hygienic Guide*, the effect of eye contact with nickel carbonyl is unknown. This substance is not known to be an eye irritant, however.
3. Evaluation of Warning Properties: Since the odor threshold of nickel carbonyl is over 1000 times greater than the permissible exposure limit, nickel carbonyl 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**

Measurement of nickel carbonyl may be done by sampling with a bubbler containing alcoholic-iodine solution, followed by chemical treatment and colorimetric analysis. The NIOSH Special Occupational Hazard Review for Nickel Carbonyl suggests a detailed method which may be employed for sampling and analyzing nickel carbonyl.

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 nickel carbonyl.

• Any clothing which becomes wet with liquid nickel carbonyl should be removed immediately and not reworn until the nickel carbonyl is removed from the clothing.

• Clothing wet with liquid nickel carbonyl should be placed in vapor-tight, sealed containers for storage until it can be discarded or until provision is made for the removal of nickel carbonyl from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nickel carbonyl, the person performing the operation should be informed of nickel carbonyl's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid nickel carbonyl contacting the eyes.

SANITATION

• Skin that becomes wet with liquid nickel carbonyl should be immediately washed or showered to remove any nickel carbonyl.

• Eating and smoking should not be permitted in areas where nickel carbonyl is handled, processed, or stored.

• Employees who handle nickel carbonyl 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 nickel carbonyl may occur and control methods which may be effective in each case:

Operation	Controls
Use in Mond process for nickel refining	Process enclosure; local exhaust ventilation; personal protective equipment
Use in plating operations on foundry patterns, steel, and electronics manufacture	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a reagent in synthesis of acrylic esters; use as a catalyst or reagent in organic synthesis	Process enclosure; local exhaust ventilation; personal protective equipment
Use in petroleum and petrochemical processing (including methanation of ammonia synthesis gas)	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 nickel carbonyl 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 nickel carbonyl gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid nickel carbonyl 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 nickel carbonyl, 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 nickel carbonyl 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 nickel carbonyl 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. Nickel carbonyl should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Nickel carbonyl may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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* SPECIAL NOTE

Nickel carbonyl appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980). 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 11, 1976.

RESPIRATORY PROTECTION FOR NICKEL CARBONYL

Condition	Minimum Respiratory Protection* Required Above 0.001 ppm
Greater than 0.001 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 nickel carbonyl. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Nickel Metal and Soluble Nickel Compounds

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 nickel compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Nickel, metallic

- Formula: Ni
- Synonyms: Nickel catalyst; Raney nickel
- Appearance and odor: Silvery gray, metallic (or darker), odorless powder.

Nickel nitrate hexahydrate

- Formula: $Ni(NO_3)_2 \cdot 6H_2O$
- Synonyms: None
- Appearance and odor: Green, odorless solid.

Nickel sulfate hexahydrate

- Formula: $NiSO_4 \cdot 6H_2O$
- Synonyms: None
- Appearance and odor: Green, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nickel metal and soluble nickel compounds is 1 milligram of nickel metal and soluble nickel compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for nickel be reduced to 0.015 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, and that nickel be regulated as an occupational carcinogen. The NIOSH Criteria Document for Inorganic Nickel and the Special Occupational Hazard Review for Nickel Carbonyl should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Metallic nickel or soluble nickel 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**

Nickel fumes are respiratory irritants and may cause pneumonitis. Skin contact may cause an allergic skin rash. Nickel and its compounds have been reported to cause cancer of the lungs and sinuses. Nickel itself is not very toxic if swallowed, but its soluble salts are quite toxic and, if swallowed, may cause giddiness and nausea. Exposure to nickel carbonyl (by inhalation or skin absorption) may cause both initial and delayed symptoms. Initial symptoms include headache, dizziness, shortness of breath, and vomiting. These symptoms generally disappear when the worker is exposed to fresh air. The delayed symptoms may develop 12 to 36 hours after exposure. The shortness of breath returns, a blue color of the skin may appear, and a fever may develop. The exposed person may become delirious. In some cases the symptoms may run together. Death 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 nickel metal and soluble nickel compounds.

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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• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nickel metal and soluble nickel 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. Persons with a history of asthma, allergies, or known sensitization to nickel metal and soluble nickel compounds would be expected to be at increased risk from exposure. Examination of the nasal cavities and lungs should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Nickel metal and soluble nickel compounds cause human lung damage and cancer of the lung. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nickel metal and soluble nickel compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Skin disease: Nickel metal and soluble compounds 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.

• **Summary of toxicology**

Metallic nickel and certain soluble nickel compounds as dust or fume cause sensitization dermatitis and probably produce cancer of the paranasal sinuses and the lung; nickel fume in high concentrations is a respiratory irritant. Severe but transient pneumonitis in two workers resulted from exposure to nickel fume; in one case, exposure was for 6 hours, and post-incident sampling suggested a nickel concentration of 0.26 mg/m^3. "Nickel itch" is a dermatitis resulting from sensitization to nickel; the first symptom is usually itching, which occurs up to 7 days before skin eruption appears. The primary skin eruption is erythematous, or follicular; it may be followed by superficial discrete ulcers, which discharge and become crusted, or by eczema; in the chronic stages, pigmented or depigmented plaques may be formed. Nickel sensitivity, once acquired, is apparently not lost; recovery from the dermatitis usually occurs within 7 days of cessation of exposure, but may take several weeks. A worker who had developed cutaneous sensitization also developed apparent asthma from inhalation of nickel sulfate; immunologic studies showed circulating antibodies to the salt, and controlled exposure to a solution of nickel sulfate resulted in decreased pulmonary function and progressive dyspnea; the possibility of developing hypersensitivity pneumonitis could not be excluded. In animals, finely divided metallic nickel was carcinogenic when introduced into the pleural cavity, muscle tissue, and subcutaneous tissues; rats and guinea pigs exposed to a concentration of 15 mg/m^3 of powdered metallic nickel developed malignant pulmonary neoplasms. Several epidemiologic studies have shown an increased incidence of cancer of the paranasal sinuses and lungs among workers in nickel refineries and factories; suspicion of carcinogenicity has been focused primarily on respirable particles of nickel, nickel subsulfide, nickel oxide, and on nickel carbonyl vapor. Many of the studies also included exposures to other suspected carcinogens.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Nickel, metallic**

1. Molecular weight: 58.7
2. Boiling point (760 mm Hg): 2730 C (4946 F)
3. Specific gravity (water = 1): 8.9
4. Vapor density (air = 1 at boiling point of metallic nickel): Not applicable
5. Melting point: 1453 C (2648 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—Nickel nitrate hexahydrate**

1. Molecular weight: 290.8
2. Boiling point (760 mm Hg): 137 C (278 F) (loses water)
3. Specific gravity (water = 1): 2.05
4. Vapor density (air = 1 at boiling point of nickel nitrate hexahydrate): Not applicable
5. Melting point: 57 C (135 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 60
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Nickel sulfate hexahydrate**

1. Molecular weight: 262.8
2. Boiling point (760 mm Hg): 103 C (217 F) (loses water)
3. Specific gravity (water = 1): 2.07
4. Vapor density (air = 1 at boiling point of nickel sulfate hexahydrate): Not applicable
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 40
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Heat (nickel only)
2. Incompatibilities: Contact of nickel with strong acids may form flammable and explosive hydrogen gas.

Contact with sulfur may cause evolution of heat. Contact of nickel nitrate with wood and other combustibles may cause fire.

3. Hazardous decomposition products: Toxic gases and vapors (such as nickel carbonyl and oxides of nitrogen) may be released in a fire involving nickel or in the decompostion of nickel compounds.

4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable

2. Minimum ignition temperature: Not available

3. Minimum explosive concentration: Not available, but nickel sponge catalyst may ignite spontaneously in air.

4. Extinguishant: Dry powder, dry sand, dry dolomite, dry graphite

• **Warning properties**

Grant states that "workers employed in nickel plating involving nickel sulfate, sulfuric acid, and chlorine are said to have developed conjunctivitis and epiphora when ventilation was poor." Since, according to Grant, "both sulfuric acid mist and chlorine gas are known to cause burning and stinging of the eyes," and since the AIHA *Hygienic Guide* states that eye contact "does not present any problem peculiar to nickel," nickel metal and soluble compounds are not treated as eye irritants.

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 treatment with nitric and perchloric acids, solution in nitric acid, and analysis with an atomic absorption spectrophotometer. An analytical method for nickel metal and soluble nickel compounds 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).
number PB 258 433).

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 powdered metallic nickel or solids or liquids containing soluble nickel compounds.

• If employees' clothing may have become contaminated with powdered metallic nickel or solid soluble nickel compounds, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with metallic nickel or soluble nickel compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of metallic nickel or soluble nickel compounds from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the metallic nickel or soluble nickel compounds, the person performing the operation should be informed of these substances's hazardous properties.

• Non-impervious clothing which becomes contaminated with metallic nickel or soluble nickel compounds should be removed promptly and not reworn until the metallic nickel or soluble nickel compounds are removed from the clothing.

SANITATION

• Skin that becomes contaminated with metallic nickel or soluble nickel compounds should be promptly washed or showered with soap or mild detergent and water to remove any metallic nickel or soluble nickel compounds.

• Eating and smoking should not be permitted in areas where solids or liquids containing soluble nickel compounds are handled, processed, or stored.

• Employees who handle powdered metallic nickel or solids or liquids containing soluble nickel compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

• Areas in which exposure to nickel metal and soluble nickel compounds may occur should be identified by

signs or 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 nickel metal and soluble nickel compounds may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture and fabricating of more than 3000 alloys; use in electronic tube parts, coins heavy machinery, tools, instrument parts, magnets, food and chemical processing equipment, flatware, jet engines, automotive parts, zippers, nickel anodes, surgical and dental instruments, and cooking utensils (they aid in corrosion- and heat-resistance, enhance ductibility, and increase thermal conductivity)	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during processing and refining of ore	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of nickel-iron alloys, and non-ferrous-nickel alloys	Local exhaust ventilation; general dilution ventilation
Use during fabrication of nickel-plated materials	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in chemical synthesis as starting material of complex compounds; use as catalysts in hydrogenation of fats/ oils	General dilution ventilation
Use in textile industry in dyeing and printing; and in ceramic industry in coloring	General dilution ventilation; local exhaust ventilation
Use of metal and salts during electroplating and electroless plating	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of nickel-iron alloys and non-ferrous-nickel alloys	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.

- **Skin Exposure**

If solids or liquids containing soluble nickel compounds get on the skin, immediately flush the contaminated skin with water. If solids of liquids containing soluble nickel compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. Metallic nickel should be removed from the skin by washing with soap or mild detergent and water.

- **Breathing**

If a person breathes in large amounts of metallic nickel of soluble nickel 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. If any nickel carbonyl has been inhaled, get medical attention promptly.

- **Swallowing**

When metallic nickel or solids or liquids containing soluble nickel 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 nickel metal and soluble nickel 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 for reclamation or for disposal in a secured sanitary landfill. Liquid containing nickel should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Nickel metal and soluble nickel compounds may be disposed of in sealed containers in a secured sanitary landfill.

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* SPECIAL NOTE

Nickel metal and soluble nickel compounds appear on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding their carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

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 11, 1976.

RESPIRATORY PROTECTION FOR NICKEL METAL AND SOLUBLE COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Dust or Mist 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.
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.
1000 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.
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.

RESPIRATORY PROTECTION FOR NICKEL METAL AND SOLUBLE COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Dust, Mist, or Fume Concentration	
10 mg/m³ or less	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.
1000 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.
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 Nicotine

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: $C_{10}H_{14}N_2$
- Synonyms: 3-(1-Methyl-2-pyrrolidyl)pyridine
- Appearance and odor: Pale yellow to dark brown liquid with a slight fishy odor when warm.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nicotine is 0.5 milligram of nicotine per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nicotine 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 rapidly enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: The action of nicotine is rapid either after breathing it, swallowing it, or absorbing it through the skin. Exposure to it may cause a burning sensation of the mouth and throat, abdominal pain, nausea, vomiting, and diarrhea. It may also cause headache, sweating, dizziness, hearing and visual disturbances, confusion, weakness, and incoordination. The heart may beat irregularly or stop. Trembling and convulsions, faintness, shortness of breath, and collapse may occur which may be followed by death from respiratory paralysis. Exposure of the eyes and skin may cause irritation. Nicotine has caused abnormalities in the offspring of laboratory animals.

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 nicotine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nicotine 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 nervous system and cardiovascular system should be stressed.

2. Periodic Medical Examination: The aforementioned medical examination should be repeated on an annual basis.

- **Summary of toxicology**

Nicotine in solution causes a transient stimulation, followed by depression or paralysis of the central nervous system, peripheral autonomic ganglia, and nerve endings in skeletal muscle; it also directly stimulates smooth muscle. Many fatal human cases of nicotine intoxication have occurred, usually as a result of accidental or suicidal ingestion of nicotine insecticides. Nicotine is readily absorbed through the skin; in fatal cases of intoxication, death nearly always occurs within 1 hour and has occurred within 1 minute; the fatal adult dose is about 60 mg. Symptoms include nausea, salivation, abdominal pain, vomiting, diarrhea, cold sweat, headache, dizziness, disturbed hearing and vision, confusion, weakness, and incoordination. Initially, respiration is deep and rapid, blood pressure is elevated, and the pulse is slow; intense vagal stimulation may cause transient cardiac standstill or paroxysmal atrial fibrillation; the pupils are generally constricted. Excitation of the central nervous system results in tremor and sometimes clonic-tonic convulsions. As central nervous system

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
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depression ensues the pupils dilate, the blood pressure falls, and the pulse becomes rapid and often irregular; faintness, prostration, dyspnea, and paralysis of respiratory muscles are followed by death. Recovery usually occurs if the victim survives 1 to 4 hours. Skeletal system malformations occurred in the offspring of pregnant mice injected subcutaneously with nicotine between days 9 to 11 of pregnancy.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 162
  2. Boiling point (760 mm Hg): 266 C (511 F)
  3. Specific gravity (water = 1): 1.0
  4. Vapor density (air = 1 at boiling point of nicotine): 5.6
  5. Melting point: −79 C (−110 F)
  6. Vapor pressure at 20 C (68 F): 0.0425 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions below 60 C (140 F)
  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. Contact with strong acids may cause violent spattering.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nicotine.
  4. Special precautions: Nicotine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 95 C (203 F) (calculated)
  2. Autoignition temperature: 244 C (471 F)
  3. Flammable limits in air, % by volume: Lower: 0.7; Upper: 4.0
  4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical
- **Warning properties**
  1. Odor Threshold: No quantitative information is available.
  2. Eye Irritation Level: Grant reports one case where exposure caused "a severe pain, much conjunctival reaction and corneal infiltration. Eventually the eye healed with partial opacification of the cornea."
  3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of nicotine, 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 nicotine on resin with subsequent desorption with ethyl acetate and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nicotine may be used. An analytical method for nicotine 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).
404).

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 nicotine.
- Clothing which has had any possibility of being contaminated with liquid nicotine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nicotine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nicotine, the person performing the operation should be informed of nicotine's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid nicotine, 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 liquid nicotine should be removed immediately and not reworn until the nicotine 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 nicotine contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid nicotine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid nicotine should be immediately washed or showered with soap or mild detergent and water to remove any nicotine.

• Eating and smoking should not be permitted in areas where liquid nicotine is handled, processed, or stored.

• Employees who handle liquid nicotine 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 nicotine may occur and control methods which may be effective in each case:

Operation	Controls
Application as a pesticide and fumigant on vegetable crops, fruit, grasses and turf, and greenhouse plants and crops	Personal protective equipment
Formulation of pesticide products and fumigants	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Liberation as a by-product during tobacco processing and manufacture of tobacco products	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Extraction and handling of nicotine	Process enclosure; local exhaust ventilation; general mechanical 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 nicotine or solutions of nicotine 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 nicotine or solutions of nicotine get on the skin, immediately flush the contaminated skin with water. If liquid nicotine or solutions of nicotine soak through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of nicotine, 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 nicotine or solutions of nicotine 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 nicotine 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:

Nicotine 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 NICOTINE

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.
25 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
35 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 35 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 nicotine; 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 35 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Nitric Acid

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: HNO_3
- Synonyms: Aqua fortis; white fuming nitric acid (WFNA); red fuming nitric acid (RFNA); hydrogen nitrate
- Appearance and odor: Colorless, yellow, or red fuming liquid with a suffocating, acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitric acid is 2 parts of nitric acid per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of nitric acid per cubic meter of air (mg/m³). NIOSH has recommended a permissible exposure limit of 2 ppm averaged over a work shift of up to ten hours per day, forty hours per week. The NIOSH Criteria Document for Nitric Acid should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitric acid 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: Nitric acid vapor or mist is an irritant of the eyes, nose, throat, and skin. Liquid nitric acid or high concentrations of nitric acid vapor may cause severe burns of the eyes with permanent damage. Liquid nitric acid or high concentrations of nitric acid vapor may produce skin burns and ulcers. Nitric acid may stain the skin a bright yellow. Exposure to high concentrations of nitric acid vapor may cause severe breathing difficulties which may be delayed in onset and may also cause pneumonia. Swallowing nitric acid may cause burns of the mouth, throat, and stomach.

2. Long-term Exposure: Repeated or prolonged exposure to nitric acid mists or strong concentrations of nitric acid vapors may cause erosion of the exposed teeth.

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 nitric acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitric acid 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 eyes, respiratory tract, skin, and teeth should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Nitric acid causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nitric acid is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Eye disease: Nitric acid is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—Skin disease: Weak nitric acid 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.

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. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis or at some other frequency to be determined by the responsible physician.

• **Summary of toxicology**

Nitric acid vapor or mist is an irritant of the eyes, mucous membranes, and skin. When nitric acid is exposed to air or comes in contact with organic matter, it decomposes to yield a mixture of toxic oxides of nitrogen, including nitric oxide and nitrogen dioxide. Exposure to high concentrations of nitric acid vapor or mist causes pneumonitis and pulmonary edema which may be fatal; onset of symptoms may be delayed for 4 to 30 hours. In contact with the eyes, the liquid produces severe burns which may result in permanent damage and visual impairment. On the skin, the liquid or concentrated vapor produces immediate, severe and penetrating burns; concentrated solutions cause deep ulcers and stain the skin a bright yellow or yellowish-brown color. The vapor and mist may erode the exposed teeth. Ingestion of the liquid will cause immediate pain and burns of the mouth, esophagus, and gastrointestinal tract.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 63 (solute)

2. Boiling point (760 mm Hg): 121.6 C (251 F) (for "constant boiling," 68%); 84 C (183 F) (white fuming nitric acid); 60 C (140 F) (red fuming nitric acid)

3. Specific gravity (water = 1): 1.41 (constant boiling); 1.5 (white fuming); 1.55 (red fuming)

4. Vapor density (air = 1 at boiling point of nitric acid): 2– 3 approximately

5. Melting point: –41 C (–42 F) (for "constant boiling," 68%); –41.6 C (–43 F) (white fuming); –52 C (–61 F) (red fuming)

6. Vapor pressure at 20 C (68 F): 2.9 mm Hg (HNO_3) (constant boiling), 2.6 mm Hg (H_2O) (constant boiling); 62 mm Hg (white fuming); 103 mm Hg (red fuming)

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: Elevated temperatures may cause containers to burst and liberate toxic oxides of nitrogen.

2. Incompatibilities: Reacts explosively with combustible organic or readily oxidizable materials such as wood, turpentine, metal powders, hydrogen sulfide, etc. Contact with strong bases may cause violent spattering.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when nitric acid decomposes.

4. Special precautions: Nitric acid will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible, but is a strong oxidizer.

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of nitric acid.

2. Eye Irritation Level: The AIHA *Hygienic Guide*, concerning eye contact with nitric acid, states that "nitric acid produces very severe immediate damage which may result in permanent damage and visual impairment."

3. Other Information: The AIHA *Hygienic Guide* notes that "'nitrous fumes,' expressed in terms of nitrogen dioxide, may cause immediate irritation of the throat at concentrations as low as 62 ppm."

4. Evaluation of Warning Properties: Patty points out that "nitric acid manufacture is more hazardous than hydrochloric acid manufacture in that . . . the oxides of nitrogen have inadequate warning properties in low, toxic concentrations." For the purposes of this guideline, nitric acid 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**

Nitric acid may be measured by collection of nitric acid in a midget impinger, followed by ultraviolet spectrophotometric analysis. An analytical method for nitric acid is in the *NIOSH Manual of Analytical Methods*, 2nd

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 nitric acid or liquids containing nitric acids having a pH equal to or less than 2.5.

• 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 nitric acid having a pH greater than 2.5.

• Clothing contaminated with nitric acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitric acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitric acid, the person performing the operation should be informed of nitric acid's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid nitric acid or solutions containing nitric acid having a pH equal to or less than 2.5, 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 nitric acid should be removed immediately and not reworn until the nitric acid 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 nitric acid or solutions containing nitric acid contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid nitric acid or solutions containing nitric acid having a pH equal to or less than 2.5, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with nitric acid should be immediately washed or showered to remove any nitric acid.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitric acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in metallurgy as a pickling agent; in metal refining, ore recovery, metal etching, and photoengraving	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in acidulation of phosphate rock and manufacture of nitrogen solutions for use in fertilizer industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a laboratory reagent; in wood pulping industry	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during inorganic synthesis in manufacture of fertilizers, explosives, herbicides, antibiotics, meat-curing, pickling, ceramics, and pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during organic synthesis in manufacture of nitrating and oxidizing agents, nylons, foams, lubricants, insecticides, dyes, explosives, photographic films, lacquers, and celluloids	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 nitric acid or strong concentrations of nitric acid vapors 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 nitric acid or strong concentrations of nitric acid vapors get on the skin, immediately flush the contaminated skin with water. If nitric acid soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of nitric acid, 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 nitric acid has been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the nitric acid. Do not attempt to make the exposed person vomit. 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 nitric acid is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Flush with copious quantities of water and neutralize with alkaline material (such as soda ash, lime, etc)..

• Waste disposal method:

Nitric acid may be disposed of by neutralizing with water and alkaline material (such as soda ash, lime, etc). and disposing in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR NITRIC ACID

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate or Vapor Concentration	
250 mg/m³ or less	A chemical cartridge respirator with a full facepiece providing protection against nitric acid.**
	A gas mask with a chin-style or a front- or back-mounted organic vapor canister providing protection against nitric acid.
	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 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	Any gas mask containing non-oxidizable sorbents and providing protection against nitric acid.
	Any escape self-contained breathing apparatus.

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

**Nitric acid is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore and should not be used to provide protection against nitric acid. Only non-oxidizable sorbents are allowed.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitric acid; 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 250 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Nitric 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: NO
- Synonyms: Nitrogen monoxide
- Appearance and odor: Colorless gas with a sharp, sweet odor. In high concentrations, nitric oxide turns brown rapidly in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitric oxide is 25 parts of nitric oxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 30 milligrams of nitric oxide per cubic meter of air (mg/m³). NIOSH has recommended a permissible exposure limit of 25 ppm (30 mg/m³) averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Oxides of Nitrogen should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitric oxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Nitric oxide changes into nitrogen dioxide in air. Nitrogen dioxide is more toxic than nitric oxide and may cause severe breathing difficulties which may be delayed in onset. Nitrogen dioxide may also cause irritation of the eyes, nose, throat, and wet skin. Exposure of animals to nitric oxide has caused drowsiness, unconsciousness, and 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 nitric oxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitric 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 central nervous system, respiratory tract, and cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Exposure to nitric oxide involves simultaneous exposure to nitrogen dioxide which causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Exposure to nitric oxide involves simultaneous exposure to nitrogen dioxide which is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis or as otherwise indicated by the responsible physician.

- **Summary of toxicology**

Nitric oxide (NO) causes narcosis in animals. Exposure of mice to 2500 ppm for 6 or 7 minutes caused narcosis, and death occurred within 12 minutes. Some early reports attributed the toxicity of nitric oxide to the formation of methemoglobin; however, more recent studies indicate that nitric oxide reacts in vitro with normal (ferrous) hemoglobin but in exposed animals this interaction does not occur and no methemoglobin is

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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formed. Nitric oxide is converted spontaneously in air to nitrogen dioxide; hence, some of the latter gas is invariably present whenever nitric oxide is found in the air. At concentrations below 50 ppm, however, this reaction is slow, and frequently substantial concentrations of nitric oxide may occur with negligible quantities of nitrogen dioxide. Nitrogen dioxide may cause delayed pulmonary edema and irritation of the eyes, nose, throat, and wet skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 30
2. Boiling point (760 mm Hg): −152 C (-241 F)
3. Specific gravity (water = 1): 1.27 (at boiling point)
4. Vapor density (air = 1 at boiling point of nitric oxide): 1.0
5. Melting point: −164 C (−263 F)
6. Vapor pressure at 20 C (68 F): 26,000 mm Hg (500 psig, cylinder pressure)
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
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 all combustible materials, chlorinated hydrocarbons, ammonia, carbon disulfide, many metals, fluorine, and ozone may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when nitric oxide decomposes.
4. Special precautions: Nitric oxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but strong oxidizing agent.

- **Warning properties**

1. Odor Threshold: May gives odor thresholds for nitric oxide of 0.3 ppm and 1 ppm.
2. Eye Irritation Level: According to Patty, nitric oxide is not an irritant. It is oxidized in air to NO_2, however, and NO_2 is known to produce eye irritation.
3. Evaluation of Warning Properties: Since the odor threshold of nitric oxide is well below the permissible exposure limit, nitric oxide 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**

Nitric oxide may be measured by the collection of nitric oxide on a solid sorbent, followed by extraction with triethanolamine and subsequent spectrophotometric analysis. Detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitric oxide may be used. An analytical method for nitric oxide 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).

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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 nitric oxide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation of fumes caused by direct combination of nitrogen and oxygen at elevated temperatures; action of dilute nitric acid on some metals; oxidation of nitrogenous materials	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Use as an intermediate in synthesis of nitric acid, acrylonitrile, hydroxylamine, nitrosyl halides, nitrosyl hydrogen sulfate, nitrogen dioxide	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as decomposition agent in certain gaseous products; additive to rocket propellants; bleaching of rayon; laboratory research	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 nitric 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.

• **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 nitric oxide is leaked or released in hazardous concentrations, the following steps should be taken:

1. Ventilate area of leak or release to disperse the 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.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Nitric Oxide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR NITRIC OXIDE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Gas Concentration	
100 ppm or less	Any chemical cartridge respirator with a full facepiece and cartridge(s) containing non-oxizidable sorbents and providing protection against nitric oxide.**
	A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against nitric oxide.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
Greater than 100 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-oxidizable sorbents and providing protection against nitric oxide.
	Any escape self-contained breathing apparatus.

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

**Nitric oxide is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore and should not be used to provide protection against nitric oxide. Only non-oxidizable sorbents are allowed.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitric oxide; 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 100 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for p-Nitroaniline

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: $C_6H_6N_2O_2$
- Synonyms: Azoic diazo component 37; para-nitroaniline; 4-nitroaniline; para-aminonitrobenzene; PNA; 1-amino-4-nitrobenzene; fast red 2G base; fast red GG base
- Appearance and odor: Yellow crystals with a pungent, faint, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-nitroaniline is 1 part of p-nitroaniline per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of p-nitroaniline per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Nitroaniline can affect the body if it comes in contact with the skin or eyes, is inhaled, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: p-Nitroaniline may cause a darkening or bluish coloring of the lips ("blue lip") and of the skin. Irritation of the nose and throat, headache, dizziness, weakness, nausea, shortness of breath, and rapid beating of the heart may occur. The overexposed person may become unconscious, cease breathing, and die.

2. Long-term Exposure: Prolonged overexposure may produce blue-colored lips and skin, and difficult breathing.

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 p-nitroaniline.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-nitroaniline 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, liver, and cardiovascular system should be stressed.

—A complete blood count: p-Nitroaniline has been shown to cause methemoglobinemia. Persons with blood disorders may be at increased risk from exposure. 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.

—Liver function tests: Since liver damage has been observed in humans exposed to p-nitroaniline, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

p-Nitroaniline absorption, whether from inhalation of the vapor or absorption of the solid through skin, causes anoxia due to the formation of methemoglobin; jaundice and anemia have been reported. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the

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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intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, nose, and ear lobes, and is usually recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. The individual usually feels well, has no complaints, and is insistent that nothing is wrong until the methemoglobin concentration approaches approximately 40%. At concentrations of over 40% there usually is weakness and dizziness; up to a 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. Ingestion of alcohol aggravates the toxic effects of p-nitroaniline. The substance is mildly irritating to the eyes and may cause some corneal damage.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 138
  2. Boiling point (760 mm Hg): 336 C (637 F)
  3. Specific gravity (water = 1): 1.437
  4. Vapor density (air = 1 at boiling point of p-nitroaniline): 4.76
  5. Melting point: 146 C (293 F)
  6. Vapor pressure at 20 C (68 F): 0.00015 mm Hg
  7. Solubility in water, g/100 g water at 18.5 C (65 F): 0.08 (slight)
  8. Evaporation rate (butyl acetate = 1): 22.6
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Strong oxidizers and moisture may result in spontaneous heating.
  3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide and carbon monoxide) may be released in a fire involving p-nitroaniline.
  4. Special precautions: Liquid p-nitroaniline will attack some forms of plastics, coatings, and rubber.
- **Flammability**
  1. Flash point: 199 C (390 F) (closed cup)
  2. Autoignition temperature: 180 C (356 F)
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Dry chemical and carbon dioxide for small fires.
- **Warning properties**
  1. Odor Threshold: The Manufacturing Chemists Association (MCA) states that p-nitroaniline is odorless.
  2. Eye Irritation Level: p-Nitroaniline, according to the MCA, "is mildly irritating to the eyes and may cause some corneal damage." For the purposes of this guideline, quarter- and half-facepiece respirators are allowed up to 60 mg/m^3 (PF—10).
  3. Evaluation of Warning Properties: Since the MCA states that p-nitroaniline is odorless and is only mildly irritating to the eyes, it is treated as a material with poor warning properties. The concentration in saturated air at 20 C could result in a significant exposure relative to the permissible 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**

An analytical method for p-nitroaniline 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 solid p-nitroaniline or liquids containing p-nitroaniline.
- If employees' clothing may have become contaminated with solid p-nitroaniline, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with p-nitroaniline should be placed in closed containers for storage until it can be

discarded or until provision is made for the removal of p-nitroaniline from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the p-nitroaniline, the person performing the operation should be informed of p-nitroaniline's hazardous properties.

- Where exposure of an employee's body to solid p-nitroaniline or liquids containing p-nitroaniline 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 p-nitroaniline should be removed immediately and not reworn until the p-nitroaniline is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid p-nitroaniline or liquids containing p-nitroaniline may contact the eyes.

SANITATION

- Skin that becomes contaminated with p-nitroaniline should be immediately washed or showered with soap or mild detergent and water to remove any p-nitroaniline.
- Workers subject to skin contact with solid p-nitroaniline should wash any areas of the body which may have contacted p-nitroaniline at the end of each work day.
- Eating and smoking should not be permitted in areas where solid p-nitroaniline is handled, processed, or stored.
- Employees who handle solid p-nitroaniline or liquids containing p-nitroaniline 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 p-nitroaniline may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use in synthesis and subsequent product preparation, such as grinding, containerization, etc.	Process enclosure; local exhaust ventilation; butyl rubber protective clothing; medical supervision; work force rotation; whole-body protection
Liberation during production of p-phenylenediamine; during production of intermediates for dyestuff manufacture; during antioxidation and antiozonation operations in rubber manufacture	Process enclosure; local exhaust ventilation; butyl rubber protective clothing; medical supervision; work force rotation; whole-body protection
Liberation during use as a gasoline-gum inhibitor; during use as an intermediate in pharmaceutical synthesis	Process enclosure; local exhaust ventilation; butyl rubber protective clothing; medical supervision; work force rotation; whole-body protection

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-nitroaniline or liquids containing p-nitroaniline get 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 p-nitroaniline or liquids containing p-nitroaniline get on the skin, immediately flush the contaminated skin with water. If p-nitroaniline or liquids containing p-nitroaniline soak through the clothing, remove the clothing immediately and flush the skin with water. If solid p-nitroaniline penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention as soon as possible.

- **Breathing**

If a person breathes in large amounts of p-nitroaniline, 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-nitroaniline 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 p-nitroaniline 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:

p-Nitroaniline may be disposed of:

1. By making packages of p-nitroaniline 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-nitroaniline in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR P-NITROANILINE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Particulate and Vapor Concentration	
60 mg/m³ (10 ppm) or less	Any supplied-air respirator. Any self-contained breathing apparatus.
300 mg/m³ (50 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 300 mg/m³ (50 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 Nitrobenzene

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: $C_6H_5NO_2$
- Synonyms: Nitrobenzol; oil of mirbane
- Appearance and odor: Pale yellow to dark brown, oily liquid with an odor like black paste shoe polish. It can be a solid at temperatures below 5.1 C (41 F).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrobenzene is 1 part of nitrobenzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of nitrobenzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrobenzene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It is readily absorbed through the skin, either as liquid or vapor. Even a small amount absorbed from clothes or shoes may cause toxic symptoms.

- **Effects of overexposure**

1. Short-term Exposure: Nitrobenzene affects the ability of blood to carry oxygen. A bluish discoloration of the skin may occur with headache, irritability, dizziness, weakness, nausea, vomiting, shortness of breath, drowsiness, and unconsciousness. If treatment is not given promptly, death may occur. The onset of symptoms may be delayed. Direct contact with the eyes or skin may cause mild irritation. Ingestion of alcohol may cause aggravation of symptoms.

2. Long-term Exposure: Repeated or prolonged exposure to nitrobenzene may cause anemia. An allergic skin rash may occur.

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 nitrobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrobenzene 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, liver, kidneys, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Nitrobenzene has been shown to cause methemoglobinemia and may cause anemia. Those with blood disorders may be at increased risk from exposure. 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. Observe for Heinz bodies.

—Urinalysis: The presence of p-nitrophenol and p-aminophenol in the urine is an indication of exposure to nitrobenzene.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Nitrobenzene absorption, whether from inhalation of the vapor or absorption of the liquid through skin, causes anoxia due to the formation of methemoglobin; chronic exposure produces anemia. In rabbits given

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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subcutaneous injections of 0.75 g of nitrobenzene there was methemoglobin, sulfhemoglobin, Heinz body formation in erythrocytes, a marked decrease in hematocrit and hemoglobin levels, reticulocytosis, and mild damage to the liver and kidney. Vapor concentrations near 40 ppm resulted in intoxication of workers; exposure to vapor concentrations averaging 6 ppm caused headache and vertigo; small amounts of methemoglobin and sulfhemoglobin and some Heinz bodies were found in the blood. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, often recognized by fellow workers. Cyanosis often occurs when the methemogoblin concentration is 15% or more. The individual may feel well, have no complaints, and may insist that nothing is wrong until the methemoglobin concentration approaches approximately 40%. At methemoglobin concentrations of over 40% there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. Ingestion of alcohol aggravates the toxic effects of nitrobenzene. p-Nitrophenol and p-aminophenol are metabolites of nitrobenzene, and their presence in the urine is an indication of exposure. Nitrobenzene is mildly irritating to the eyes; it may produce dermatitis due to primary irritation or sensitization.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 123.1
  2. Boiling point (760 mm Hg): 211 C (412 F)
  3. Specific gravity (water = 1): 1.2
  4. Vapor density (air = 1 at boiling point of nitrobenzene): 4.3
  5. Melting point: 5.1 C (41 F)
  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): 0.19
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with concentrated nitric acid or nitrogen tetroxide may cause fires and explosions. Contact with caustics and chemically active metals such as tin and zinc can cause evolution of much heat and fumes.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitrobenzene.
  4. Special precautions: Liquid nitrobenzene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 88 C (190 F) (closed cup)
  2. Autoignition temperature: 482 C (900 F)
  3. Flammable limits in air, % by volume: Lower: 1.8
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Both Stern and May report that the odor threshold of nitrobenzene is 1.9 ppm.
  2. Eye Irritation Level: Browning states that nitrobenzene causes "only slight transient (eye) irritation." Grant states that "the most reliably established ocular effects are secondary to discoloration of the blood from methemoglobinemia, and consist of brown discoloration of the vessels of the fundus and the conjunctiva."
  3. Evaluation of Warning Properties: Since the odor threshold of nitrobenzene is within twice the permissible exposure limits, nitrobenzene 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 nitrobenzene in an adsorption tube containing silica gel, followed by desorption with methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrobenzene may be used. An analytical method for nitrobenzene 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 liquid nitrobenzene.

• If employees' clothing has had any possibility of being contaminated with liquid nitrobenzene, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with liquid nitrobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitrobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitrobenzene, the person performing the operation should be informed of nitrobenzene's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid nitrobenzene, 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 nitrobenzene should be removed immediately and not reworn until the nitrobenzene is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid nitrobenzene may contact the eyes.

SANITATION

• Skin that becomes contaminated with nitrobenzene should be immediately washed or showered with soap or mild detergent and water to remove any nitrobenzene.

• Workers subject to skin contact with liquid nitrobenzene should wash with soap or mild detergent and water any areas of the body which may have contacted nitrobenzene at the end of each work day.

• Eating and smoking should not be permitted in areas where liquid nitrobenzene is handled, processed, or stored.

• Employees who handle liquid nitrobenzene 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 nitrobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in production of chemical intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in solvent refining of lubricating oils; use in production of intermediates in synthesis of rubber chemicals, photographic chemicals, explosives, liquid propellants, and pharmaceuticals	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a solvent in specialized surface coatings; use as a solvent in organic synthesis	Process enclosure; local exhaust ventilation; personal protective equipment
Use as perfume in manufacture of toilet and household soaps; use in synthesis of insecticides and germicides	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 nitrobenzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid nitrobenzene gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid nitrobenzene 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 nitrobenzene, 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 nitrobenzene 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 or solid nitrobenzene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. 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.
3. If in the solid form, allow to melt and handle as indicated in (2) above.

• Waste disposal methods:

Nitrobenzene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in sealed containers 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 NITROBENZENE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
10 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
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.
200 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 200 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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitrobenzene; 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 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

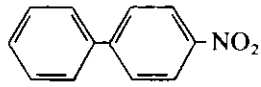
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 4-NITROBIPHENYL POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 4-nitrobiphenyl 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:** $C_{12}H_9NO_2$
- **Structure:**



- **Synonyms:** p-Nitrobiphenyl; p-nitrodiphenyl; 4-nitrodiphenyl; p-phenyl-nitrobenzene; 4-phenylnitrobenzene; PNB
- **Identifiers:** CAS 92-93-3; RTECS DV560000; DOT not assigned
- **Appearance and odor:** White to yellow needle-like crystals with a sweetish odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 199.22
2. Boiling point (at 760 mmHg): 340°C (644°F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of 4-nitrobiphenyl): 6.87
5. Melting point: 113.8°C (236.8°F)
6. Insoluble in water

- **Reactivity**

Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen) may be released in a fire involving 4-nitrobiphenyl.

- **Flammability**

1. Flash point: 143°C (290°F) (closed cup)
2. Extinguishant: Water or foam (may cause frothing)
3. 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-nitrobiphenyl; however, the OSHA standard requires implementation of stringent controls wherever 4-nitrobiphenyl or solid or liquid mixtures containing at least 0.1% by weight or volume of 4-nitrobiphenyl 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 1910.1003, 4-Nitrobiphenyl. 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-nitrobiphenyl as an A1 substance (confirmed human carcinogen). The ACGIH recommends that virtually no exposure to 4-nitrobiphenyl be permitted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

Effects on animals: Chronic oral administration of 4-nitrobiphenyl to dogs produced bladder cancer. In rats exposed to 4-nitrobiphenyl, the chemical is metabolically converted to 4-aminodiphenyl, a recognized animal and human bladder carcinogen.

2. *Effects on humans:* Because of the known metabolic conversion of 4-nitrobiphenyl to 4-aminodiphenyl in animals and the potential conversion in humans, it is not possible to separate the exposure to either substance; thus, the carcinogenicity of 4-nitrobiphenyl alone has not been documented in human epidemiologic studies. Bladder cancer is strongly associated

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with occupational exposure to 4-aminodiphenyl, and 4-nitrobiphenyl is used in the production of 4-aminodiphenyl.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 4-nitrobiphenyl can cause headache, lethargy, painful urination, and blood or pus in the urine.

2. *Long-term (chronic):* Exposure to 4-nitrobiphenyl can cause headache, weakness, dizziness, a feeling of euphoria, breathing difficulty (dyspnea), impaired muscular coordination (ataxia), blood or pus in the urine, and painful, difficult, or frequent 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-nitrobiphenyl, 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-nitrobiphenyl. 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 or urinary tract. 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-nitrobiphenyl. 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-nitrobiphenyl 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-nitrobiphenyl 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-nitrobiphenyl may also be used if available. A detailed sampling and analytical method for 4-nitrobiphenyl may be found in the *NIOSH Manual of Analytical Methods* (method number 273).

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-nitrobiphenyl 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-nitrobiphenyl 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 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-nitrobiphenyl 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-nitrobiphenyl from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 4-nitrobiphenyl'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-nitrobiphenyl 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 1910.1003:

Areas where 4-nitrobiphenyl 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-nitrobiphenyl, local and systemic toxicity, the specific nature of the operation that 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-nitrobiphenyl which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of 4-nitrobiphenyl into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where 4-nitrobiphenyl 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-nitrobiphenyl 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-nitrobiphenyl from materials, equipment, and the decontamination facility.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to 4-nitrobiphenyl 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-nitrobiphenyl

Operations	Controls
During use in the production of rocket fuel; during use as an industrial solvent (especially in the fibers and plastics industries), as an oxidant, and as an additive in lubricants	Process enclosure, restricted access, local exhaust ventilation where appropriate, 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-nitrobiphenyl, 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-nitrobiphenyl, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 4-nitrobiphenyl 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-nitrobiphenyl, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 4-nitrobiphenyl gets on the skin, wash it immediately with soap and water. If 4-nitrobiphenyl 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 areas affected by 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-nitrobiphenyl 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-nitrobiphenyl may be collected and placed in an appropriate container.
4. 4-Nitrobiphenyl solid or liquid 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 mopping of 4-nitrobiphenyl 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.
5. For small quantities of liquids containing 4-nitrobiphenyl, absorb on paper towels and place in an appropriate container.
6. Large quantities of liquids containing 4-nitrobiphenyl 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 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-nitrobiphenyl

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 p-Nitrochlorobenzene

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-$ClC_6H_4NO_2$
- Synonyms: PNCB; 4-chloronitrobenzene; PCNB; p-chloronitrobenzene; 1-chloro-4-nitrobenzene
- Appearance and odor: Yellow solid with a sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-nitrochlorobenzene is 1 milligram of p-nitrochlorobenzene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Nitrochlorobenzene can affect the body if it is inhaled, comes in contact with the eyes or skin, or swallowed. It is readily absorbed through the skin. Even a small amount absorbed from clothes or shoes may cause toxic symptoms.

- **Effects of overexposure**

1. Short-term Exposure: p-Nitrochlorobenzene affects the ability of the blood to carry oxygen normally. A bluish discoloration of the skin may occur with headache, irritability, dizziness, weakness, nausea, vomiting, shortness of breath, drowsiness, and unconsciousness. If treatment is not given promptly, death may occur. The onset of symptoms may be delayed. p-Nitrochlorobenzene may also cause an unpleasant taste. The ingestion of alcohol may cause increased susceptibility to the effects of p-nitrochlorobenzene. The earliest effect may be a bluish color of the skin, especially of the lips. If the lack of oxygen becomes severe, drowsiness, headache, nausea, and vomiting may occur. If oxygen lack is very severe, it may cause unconsciousness and even death. It will also cause the mouth and breath to smell of bitter almonds.

2. Long-term Exposure: Repeated or prolonged exposure to p-nitrochlorobenzene may cause anemia and 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 p-nitrochlorobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-nitrochlorobenzene 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, liver, kidneys, and cardiovascular system should be stressed.

—A complete blood count: p-Nitrochlorobenzene has been shown to cause methemoglobinemia and anemia. Those with blood disorders may be at increased risk from exposure. 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. Observe for Heinz bodies.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Absorption of p-nitrochlorobenzene, whether by inhalation of vapor or dust or by absorption of the solid through the skin, causes anoxia due to the formation of methemoglobin. Application of the solid dissolved in

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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.

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

olive oil to the skin of rabbits caused methemoglobinemia, the formation of Heinz bodies in erythrocytes, anemia, hematuria, and hemoglobinuria. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and may be recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. The individual may feel well, have no complaints, and may insist that nothing is wrong until the methemoglobin concentration approaches approximately 40%. At methemoglobin concentrations of over 40% there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. The ingestion of alcohol aggravates the toxic effects of p-nitrochlorobenzene. Four workers exposed for a period of 2 to 4 days to an unmeasured concentration of the vapor developed methemoglobinemia; an unpleasant taste in mouth and anemia developed during the week after exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 157.6
2. Boiling point (760 mm Hg): 242 C (468 F)
3. Specific gravity (water = 1): 1.37
4. Vapor density (air = 1 at boiling point of p-nitrochlorobenzene): 5.4
5. Melting point: 83 C (181 F)
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): 0.003
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 oxides of nitrogen, hydrogen chloride, and carbon monoxide) may be released in a fire involving p-nitrochlorobenzene.
4. Special precautions: Liquid p-nitrochlorobenzene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 127 C (261 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**

According to Grant, nitrochlorobenzene (NCB), "like nitrobenzene, has been observed to cause methemoglobinemia, with discoloration of the conjunctiva reflecting the change in the color of the blood." NCB is not known to be an eye irritant, however.

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 p-nitrochlorobenzene in an absorption tube containing silica gel, followed by desorption with methanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure p-nitrochlorobenzene may be used. An analytical method for p-nitrochlorobenzene 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 p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene, where skin contact may occur.

• If employees' clothing may have become contaminated with p-nitrochlorobenzene, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with p-nitrochlorobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of p-nitrochlorobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the p-nitrochlorobenzene, the person performing the operation should be informed of p-nitrochlorobenzene's hazardous properties.

• Where exposure of an employee's body to liquids containing p-nitrochlorobenzene 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 wet with liquids containing p-nitrochlorobenzene should be removed immediately and not reworn until the p-nitrochlorobenzene is removed from the clothing.

SANITATION

• Skin that becomes wet with liquids containing p-nitrochlorobenzene should be immediately washed or showered with soap or mild detergent and water to remove any p-nitrochlorobenzene.

• Skin that becomes wet with p-nitrochlorobenzene should be promptly washed or showered with soap or mild detergent and water to remove any p-nitrochlorobenzene.

• Workers subject to skin contact with p-nitrochlorobenzene should wash with soap or mild detergent and water any areas of the body which may have contacted p-nitrochlorobenzene at the end of each work day.

• Eating and smoking should not be permitted in areas where p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene are handled, processed, or stored.

• Employees who handle p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene 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 p-nitrochlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in production of chemical intermediates for manufacture of pesticides, fungicides, and preservatives; production of chemical intermediates for manufacture of sulfur and azo-fast dyes; synthesis of intermediates in manufacture of pharmaceuticals, rubber chemicals, antioxidants, gasoline gum inhibitors, corrosion inhibitors, and photographic chemicals	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 p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene 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 p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If p-nitrochlorobenzene or liquids containing p-nitrochlorobenzene 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 p-nitrochlorobenzene, 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-nitrochlorobenzene or liquids containing p-nitrochlorobenzene 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 p-nitrochlorobenzene 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:

p-Nitrochlorobenzene may be disposed of:

1. By making packages of p-nitrochlorobenzene 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-nitrochlorobenzene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR p-NITROCHLOROBENZENE

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any dust and mist respirator, except single-use.
10 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.
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.
1000 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 1000 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 Health Guideline for Nitroethane

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: $C_2H_5NO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitroethane is 100 parts of nitroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 310 milligrams of nitroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitroethane 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**

In man, mild skin irritation has occured from repeated exposure of the skin. Animal exposure to nitroethane has produced irritation of the respiratory tract with breathing difficulties which may be delayed in onset. Irritation of the eyes, anesthesia, and death have also occured.

- **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 nitroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitroethane 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 nitroethane exposure.

—Chronic respiratory disease: Nitroethane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of nitroethane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Nitroethane 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: Nitroethane 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: Nitroethane 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**

Nitroethane is a mild skin irritant. In animals, nitroethane vapor is narcotic and a pulmonary irritant and also causes liver damage. Rabbits died from exposure to 5000 ppm for 3 hours; exposure to 2500 ppm for 3 hours was not fatal. Effects were lacrimation, dyspnea, pulmonary rales, and, in a few animals, pulmonary edema. Twitching and jerking movements of the head and extremities were observed; convulsions were rare and of brief duration. Stupor or narcosis at high concentra-

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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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tions was rapidly reversible. Autopsy of animals exposed to lethal concentrations showed mild to severe liver damage and non-specific changes in the kidneys. No systemic effects have been reported in humans. The liquid is a mild skin irritant due to solvent action.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 75.1
2. Boiling point (760 mm Hg): 114 C (237 F)
3. Specific gravity (water = 1): 1.05
4. Vapor density (air = 1 at boiling point of nitroethane): 2.6
5. Melting point: −90 C (−130 F)
6. Vapor pressure at 20 C (68 F): 15.6 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 4.5
8. Evaporation rate (butyl acetate = 1): 1.2

- **Reactivity**

1. Conditions contributing to instability: Overheating of closed containers may cause detonation.

2. Incompatibilities: Contact with amines, strong acids, and alkalies may sensitize nitroethane so that it will readily explode. Contact with strong oxidizers may cause fires and explosions. Mixtures of nitroethane and hydrocarbons (or other combustible materials) are highly flammable. Contact with some metal oxides may cause decomposition and development of pressure.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitroethane.

4. Special precautions: Liquid nitroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 27.8 C (82 F) (closed cup)
2. Autoignition temperature: 414 C (778 F)
3. Flammable limits in air, % by volume: Lower: 3.4; Upper: Data not available
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Patty states that "the odors of nitroparaffins are easily detectable, and concentrations below 200 ppm are disagreeable to most observers. The odor and sensory symptoms are not dependable warning properties."

2. Eye Irritation Level: The AIHA *Hygienic Guide* states that the vapors of nitroethane "are noticeably irritating at concentrations above 100 ppm but cannot be relied upon for warning properties." At 500 ppm and above, strong eye (and respiratory tract) irritation has been observed in animals.

3. Evaluation of Warning Properties: Patty states that "the odor and sensory symptoms (of the nitroparaffins) are not dependable 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 nitroethane 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 liquid nitroethane.
- Clothing wet with liquid nitroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitroethane, the person performing the operation should be informed of nitroethane's hazardous properties.
- Any clothing which becomes wet with liquid nitroethane should be removed immediately and not reworn until the nitroethane is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid nitroethane may contact the eyes.

SANITATION

• Skin that becomes wet with liquid nitroethane should be promptly washed or showered with soap or mild detergent and water to remove any nitroethane.

• Employees who handle liquid nitroethane 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 nitroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in coatings and adhesives on cellulose esters and synthetic resins	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an intermediate in synthesis of organic dyes, insecticides, pesticides, nitroplasticizers, pharmaceuticals, and other organic chemicals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a propellant; as a reaction-media fluid; as an extraction solvent in petroleum fractionation; use as a recrystallization solvent	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 nitroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid nitroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid nitroethane 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 nitroethane, 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 nitroethane 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 nitroethane 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 and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities can be collected, diluted in fuel oil, and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Liquid nitroethane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Liquid nitroethane may be disposed of by diluting with fuel oil and by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
• 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 NITROETHANE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
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 escape self-contained breathing apparatus.

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

Occupational Health Guideline for Nitrogen 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: NO_2 and N_2O_4
- Synonyms: Nitrogen tetroxide; NTO; dinitrogen tetroxide; nitrogen peroxide
- Appearance and odor: Dark brown fuming liquid or gas with a pungent, acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrogen dioxide is a ceiling of 5 parts of nitrogen dioxide per million parts of air (ppm) (*Federal Register*, Vol. 43, No. 237, pp. 57601-03, 8 December 1978). This may also be expressed as 9 milligrams of nitrogen dioxide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 1 ppm (1.8 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for Oxides of Nitrogen should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrogen 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**

Exposure to nitrogen dioxide may cause severe breathing difficulties which are usually delayed in onset and which may cause death. Recovery may be slow (2 to 3 weeks) with possible relapse and possible permanent lung damage. Pneumonia may occur. Irritation of the eyes, nose, throat, and wet skin may occur with acute exposures.

- **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 nitrogen dioxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrogen 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 tract and cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Nitrogen dioxide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nitrogen dioxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis or as otherwise indicated by the responsible physician.

- **Summary of toxicology**

Nitrogen dioxide gas is a respiratory irritant; it causes pulmonary edema and rarely, among survivors, bronchiolitis obliterans. Brief exposure of humans to concentrations of about 250 ppm causes cough, production of mucoid or frothy sputum, and increasing dyspnea. Within 1 to 2 hours the person may develop pulmonary edema with tachypnea, cyanosis, and fine crackles and wheezes throughout the lungs, and tachycardia. Alter-

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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natively, there may be only increasing dyspnea and cough over several hours, the symptoms then gradually subside over a 2- to 3-week period. The condition may then enter a second stage of abruptly increasing severity; fever and chills precede a relapse with increasing dyspnea, cyanosis, and recurring pulmonary edema. Death may occur either in the initial or second stage of the disease; a severe second stage may follow a relatively mild initial stage. The subject who survives the second stage usually recovers over 2 to 3 weeks; however, some do not return to normal, but experience varying degrees of impaired pulmonary function. The radiographic features in the acute initial stage vary from normal to those of typical pulmonary edema; most reports mention a pattern of nodular shadows on the chest film at the outset. The roentgenogram may then clear, only to show miliary mottling as the second stage commences, progressing to the development of a confluent pattern. Results of pulmonary function tests in the acute stage show reduction in lung volume and diffusing capacity; similar findings are recorded in the second stage. Pathologic examination of the acute lesion shows extensive mucosal edema and inflammatory cell exudation. The delayed lesion shows the histologic appearance of bronchiolitis obliterans; small bronchi and bronchioles contain an inflammatory exudate which tends to undergo fibrinous organization, finally obliterating the lumen. The effects expected in humans from exposure to nitrogen dioxide for 60 minutes are: 100 ppm, pulmonary edema and death; 50 ppm, pulmonary edema with possible subacute or chronic lesions in the lungs; 25 ppm, respiratory irritation and chest pain. A concentration of 50 ppm is moderately irritating to the eyes and nose; 25 ppm is irritating to some people.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 46 and 92
2. Boiling point (760 mm Hg): 21 C (70 F)
3. Specific gravity (water = 1): 1.45 (liquid)
4. Vapor density (air = 1 at boiling point of nitrogen dioxide): 2.83
5. Melting point: −11.2 C (11.8 F)
6. Vapor pressure at 20 C (68 F): 720 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions (reacts to form nitric acid and nitric oxide)
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to explode.
2. Incompatibilities: Contact with all combustible materials, chlorinated hydrocarbons, ammonia, and carbon disulfide may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when nitrogen dioxide decomposes.
4. Special precautions: Nitrogen dioxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but strong oxidizing agent.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* reports an odor threshold of 5 ppm.
2. Eye Irritation Level: According to Grant, "the gas at a concentration in approximately 70 ppm in air causes irritation of the eyes and nose evident in guinea pigs, rabbits, monkeys, and dogs during the first hour of exposure. At this concentration the gas has been lethal to most of the animals if exposed for eight hours, and under these conditions corneal opacities have been produced in the rabbits. The corneas of rabbits that survived such exposures did not improve under observation during twenty days. However, the gas at concentrations up to 20 ppm in air and exposure of four hours has produced no significant effect on the corneas of rabbits . . . . Exposure of the same magnitude repeated daily for more than a month also has not been damaging to the eye." The *Documentation of TLV's* reports that according to Patty, 10-20 ppm "were mildly irritant to the eyes . . . ."
3. Other Information: The AIHA *Hygienic Guide* states that "exposures of relatively short duration to concentrations above 5 ppm produce cough and irritation of the respiratory tract."
4. Evaluation of Warning Properties: Through its odor and irritant effects, nitrogen dioxide can be detected slightly above the recommended permissible exposure limit. For the purposes of this guideline, therefore, nitrogen dioxide 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 nitrogen dioxide. 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 gas in a reagent-filled impinger with a subsequent spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrogen dioxide may be used. An analytical method for nitrogen dioxide 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 liquid nitrogen dioxide.

• Clothing contaminated with nitrogen dioxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitrogen dioxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitrogen dioxide, the person performing the operation should be informed of nitrogen dioxide's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid nitrogen 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 nitrogen dioxide should be removed immediately and not reworn until the nitrogen 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 nitrogen dioxide contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid nitrogen dioxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with nitrogen dioxide should be immediately washed or showered to remove any nitrogen dioxide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitrogen dioxide may occur and control methods which may be effective in each case:

Operation	Controls
Use during metal surface treatment with nitric acid; in production of intermediates in manufacture of sulfuric acid, nitric acid, and fertilizers	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation of fumes during engine maintenance, synthesis of dyes, manufacture of nitrocellulose paints, lacquers, and storage of silage in agricultural operations; production and handling of rocket propellants	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation of fumes during detonation of explosives	Personal protective equipment
Use in chemical synthesis during nitration operations	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 nitrogen dioxide or strong concentrations of nitrogen dioxide 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 nitrogen dioxide or strong concentrations of nitrogen dioxide vapor get on the skin, immediately flush the contaminated skin with water. If liquid nitrogen dioxide or strong concentrations of nitrogen dioxide vapor penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of nitrogen 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**

When liquid nitrogen dioxide has been swallowed and if the person is conscious, immediately give the person large amounts of water to dilute the nitrogen dioxide. Do not attempt to make the 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 LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If nitrogen dioxide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in the liquid form, allow to vaporize.
3. If in the 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.

REFERENCES

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RESPIRATORY PROTECTION FOR NITROGEN DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration	
50 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) containing non-oxidizable sorbents and providing protection against nitrogen dioxide.** A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against nitrogen dioxide. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 50 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-oxidizable sorbents and providing protection against nitrogen dioxide. Any escape self-contained breathing apparatus.

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

**Nitrogen dioxide is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore should not be used to provide protection against nitrogen dioxide. Only non-oxidizable sorbents are allowed.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitrogen dioxide; 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 50 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Nitrogen 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: NF_3
- Synonyms: None
- Appearance and odor: Colorless gas with a moldy odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrogen trifluoride is 10 parts of nitrogen trifluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 29 milligrams of nitrogen trifluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrogen trifluoride can affect the body if it is inhaled.

- **Effects of overexposure**

There are no reports of human intoxication from nitrogen trifluoride. In animals, nitrogen trifluoride can affect the ability of the blood to carry oxygen by forming methemoglobin. In man, methemoglobin formation may cause a bluish discoloration of the skin, drowsiness, dizziness, nausea, rapid heart beat, headache, shortness of breath, and unconsciousness.

- **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 nitrogen trifluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrogen 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 blood, cardiovascular system, nervous system, liver, and kidneys should be stressed.

—A complete blood count: Nitrogen trifluoride has been shown to cause methemoglobinemia in animals. Persons with blood disorders may be at increased risk from exposure. 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. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Nitrogen trifluoride gas causes anoxia due to the formation of methemoglobin in animals. Rats died from exposure to 10,000 ppm for 60 to 70 minutes; the methemoglobin concentrations at the time of death were equivalent to 60 to 70% of available hemoglobin. Animals exposed to nearly lethal concentrations suffered severe respiratory distress and cyanosis due to methemoglobinemia; severely affected animals showed incoordination, collapse and convulsions. Rats repeatedly exposed to 100 ppm for 4-½ months appeared normal, but autopsy findings indicated injury to the liver and kidneys. There are no reports of human intoxication from nitrogen trifluoride; however, the expected effects of methemoglobinemia in humans would result from anoxia and include cyanosis, evident

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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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especially in the lips, nose, and ear lobes; other effects are weakness, dizziness, and severe headache.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 71
  2. Boiling point (760 mm Hg): −129 C (−200 F)
  3. Specific gravity (water = 1): 1.54 (liquid)
  4. Vapor density (air = 1 at boiling point of nitrogen trifluoride): 2.5
  5. Melting point: −206.8 C (−340 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): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: Particularly hazardous under pressure; can react spontaneously due to shock or heat.
  2. Incompatibilities: Contact of nitrogen trifluoride with oxidizable materials (such as ammonia, carbon monoxide, methane, hydrogen, and hydrogen sulfide), chemically active metals, and oxides (such as silica (sand)) may cause fires and explosions. Mixtures of nitrogen trifluoride and water vapor may explode when ignited by high energy sources. It can react violently with grease or oil.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible by itself, but can react explosively with reducing materials.
  2. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.
- **Warning properties**
  1. Odor Threshold: According to the *Documentation of TLV's*, "NF_3 provides no odor-warning properties at potentially dangerous levels."
  2. Eye Irritation Level: The ILO states that "nitrogen trifluoride is strikingly less irritating than elemental fluorine, chlorine trifluoride, and oxygen difluoride." Information is not available concerning the threshold of eye irritation.
  3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of nitrogen trifluoride, and since the *Documentation of TLV's* states that "NF_3 provides no odor-warning properties at potentially dangerous levels," 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**

At the time of publication of this guideline, no measurement method for nitrogen 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.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitrogen trifluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of flash cubes; use in welding, brazing, and cutting of metals using hydrogen-nitrogen trifluoride torch	Process enclosure; local exhaust ventilation; personal protective equipment
Use in research as an oxidizer for rocket and other high-energy fuels	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of tetrafluorohydrazine	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 nitrogen 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.

• **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 nitrogen trifluoride 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 in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR NITROGEN TRIFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
100 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
500 ppm or less	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 nitrogen trifluoride. Any escape self-contained breathing apparatus.

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

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR NITROGLYCERIN AND ETHYLENE GLYCOL DINITRATE

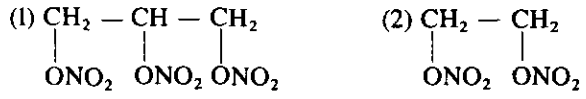
INTRODUCTION

This guideline summarizes pertinent information about nitroglycerin (NG) and ethylene glycol dinitrate (EGDN) 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 (1) nitroglycerin and (2) ethylene glycol dinitrate.

- **Formula:** (1) $C_3H_5N_3O_9$ (2) $C_2H_4N_2O_6$
- **Structure:**



- **Synonyms:** (1) Anginine, blasting gelatin, blasting oil, glonoin, glycerol trinitrate, glyceryl nitrate, glyceryl trinitrate, GTN, myocon, NG, niglycon, niong, nitric acid triester of glycerol, nitrine-TDC, nitroglycerol, nitroglyn, nitrol; (2) Dinitroglycol, EGDN, ethanediol dinitrate, ethylene dinitrate, ethylene nitrate, glycol dinitrate, nitroglycol
- **Identifiers:** (1) CAS 55-63-0; RTECS QX2100000; DOT not assigned; (2) CAS 628-96-6; RTECS KW5600000; DOT not assigned
- **Appearance and odor:** (1) Pale yellow, slightly sweet smelling oil; (2) yellowish liquid with no odor

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for (1) nitroglycerin and (2) ethylene glycol dinitrate. If not specified, data apply to both compounds.

- **Physical data**

1. Molecular weight: (1) 227.11; (2) 152.08
2. Boiling point (at 760 mmHg): (1) 256°C (493°F); (2) 197-200°C (387-392°F)
3. Explosive point: (1) 270°C (518°F); (2) 114°C (237°F)
4. Specific gravity (water = 1): (1) 1.6; (2) 1.49
5. Vapor density: (1) 7.8 (air = 1 at boiling point of NG); (2) 5.24 (air = 1 at boiling point of EGDN)
6. Melting point: (1) 13.1°C (55.1°F); (2) -22.3°C (-9°F)
7. Vapor pressure at 20°C (68°F): (1) 0.00012-0.011 mmHg; (2) 0.04 mmHg
8. (1) Slightly soluble in water; (2) insoluble in water

- **Reactivity**

1. Incompatibilities: Contact with acids, heat, or mechanical shock may result in explosion.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in an explosion involving NG or EGDN.

- **Flammability**

1. Flash point: Explodes
2. Autoignition temperature: (1) 270.4°C (518°F); (2) 195°C (383°F)
3. Class A Explosive (29 CFR 1910.109), Flammability Rating 2 (NFPA)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, NG and EGDN should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for NG and EGDN is 0.2 parts of NG or EGDN per million parts of air (ppm) [2 milligrams of NG or 1 milligram of EGDN per cubic meter of air (mg/m^3)] as a ceiling concentration which shall at no time be exceeded (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) recommended exposure limit (REL) for NG or EGDN alone or for mixtures of the two substances is 0.1 mg/m^3 as a ceiling concentration determined in any 20-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) for NG or EGDN is

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0.05 ppm (0.5 mg/m³ NG or 0.3 mg/m³ EGDN) as a time-weighted average concentration (TWA) for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational exposure limits for nitroglycerin and ethylene glycol dinitrate

	Exposure limits ppm	mg/m³
OSHA PEL		
NG ceiling (Skin)*	0.2	2
EGDN ceiling (Skin)†	0.2	1
NIOSH REL		
Ceiling (20 min)	—	0.1
ACGIH TLV®		
NG TWA (Skin)	0.05	0.5
EGDN TWA (Skin)	0.05	0.3

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† If the atmospheric concentration of EGDN exceeds 0.02 ppm, personal protection may be necessary to avoid headache.

HEALTH HAZARD INFORMATION

• Routes of exposure

NG and EGDN may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• Summary of toxicology

1. *Effects on animals:* Subchronic inhalation of EGDN by mice caused lethargy, skin damage, muscle spasms, and death due to circulatory and respiratory paralysis. In cats, subchronic or chronic inhalation or dermal administration of EGDN caused severe anemia, decreased appetite, seizures, hemorrhage of internal organs, and death. Chronic oral administration of NG to rats produced cancer of the liver. NIOSH will continue to monitor the research regarding NG to determine whether the collective evidence justifies controlling this chemical as a carcinogen.

2. *Effects on humans:* Acute inhalation or dermal exposure of workers to NG and EGDN has caused decreased systolic, diastolic, and pulse blood pressures due to vascular dilation. Chronic exposure to NG and EGDN has caused damage to the heart and reduced tolerance to alcohol. Chronic exposure to NG and EGDN, or to NG alone, followed by a brief or extended period away from exposure, has been associated with an increased incidence of sudden death.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to NG and EGDN can cause severe headache, dizziness, nausea, and heart palpitations.

2. *Long-term (chronic):* Exposure to NG and EGDN can cause severe chest pain (angina pectoris), which frequently occurs during brief periods away from work. Skin sensitization 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 NG or EGDN, 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 nervous, cardiovascular, and hematopoietic (blood-cell-forming) 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 NG or EGDN 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 disease, especially coronary artery 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 NG or EGDN. 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 nervous, hematopoietic, and cardiovascular sys-

tems 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 NG or EGDN may cause diseases of prolonged induction-latency, the need for medical surveillance may extend beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include methemoglobinemia.
2. Delayed-onset SHE's include methemoglobinemia and chest pain (angina pectoris).

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of NG and EGDN. 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 20-minute sample or a series of consecutive samples that total 20 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 NG and EGDN vapors with tenax solid sorbent tubes followed by desorption with ethanol and analysis by gas chromatography. Detector tubes or other direct-reading devices calibrated to measure NG and EGDN may also be used if available. A detailed sampling and analytical method for NG and EGDN may be found in the *NIOSH Manual of Analytical Methods* (method number 2507).

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 NG and EGDN.

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

SANITATION

Clothing which is contaminated with NG or EGDN 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 NG and EGDN from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of NG and EGDN's hazardous properties.

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

Skin that becomes contaminated with NG or EGDN 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 NG or EGDN 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 NG and EGDN 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 nitroglycerin and ethylene glycol dinitrate

Operations	Controls
During formulation and filling operations in the manufacture of industrial explosives and propellants	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the synthesis and handling of NG or EGDN; during the handling of industrial explosives	Process enclosure, local exhaust ventilation, temperature control, personal protective equipment
During the preparation and handling of dosage forms including tablets and solutions in the manufacture of pharmaceuticals	Process enclosure, 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 NG or EGDN, an eye-wash fountain should be provided within the immediate work area for emergency use.

If NG or EGDN 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 these compounds.

• **Skin exposure**
Where there is any possibility of a worker's body being exposed to NG or EGDN, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If NG or EGDN gets on the skin, wash it immediately with soap and water. If NG or EGDN 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 NG or EGDN 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 NG or EGDN, absorb on sponges or paper towels kept in a sodium carbonate solution. Remove paper towels to a secure outdoor location for burning.
4. Large quantities of liquids containing NG or EGDN may be washed with water into holding tanks where NG and EGDN can be separated. NG and EGDN should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. If in solid form, NG and EGDN may be collected using nonsparking tools and removed to a secure, outdoor location for burning.

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 nitroglycerin and ethylene glycol dinitrate

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.2 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)
Less than or equal to 0.5 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 2 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 20 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 40 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 40 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 0.1 mg/m^3 (ceiling).

Occupational Health Guideline for Nitromethane

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_3NO_2
- Synonyms: None
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitromethane is 100 parts of nitromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 250 milligrams of nitromethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitromethane 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**

In man, mild skin irritation has occurred from repeated exposure of the skin. Animal exposure to nitromethane has produced irritation of the respiratory tract, with breathing difficulties which might be delayed in onset. Irritation of the eyes, anesthesia, convulsion, and death have also occurred.

- **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 nitromethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitromethane 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 nitromethane exposure.

—Chronic respiratory disease: Nitromethane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of nitromethane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: Nitromethane 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.

—Convulsive disorders: Nitromethane causes convulsions in animals. Persons with a history of such disorders may be more susceptible to the effects of this agent.

—Kidney disease: Nitromethane 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: Nitromethane 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**

Nitromethane is a mild skin irritant due to its solvent action. In animals the vapor affects the central nervous system by causing convulsions and narcosis and is a mild pulmonary irritant. It also causes liver damage in animals. Rabbits died from exposure to 10,000 ppm for 6 hours; there was weakness, ataxia and muscular incoor-

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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dination followed by convulsions after a latent period. This concentration for 3 hours was not fatal. Autopsy of animals exposed to lethal concentrations revealed focal necrosis in the liver and moderate kidney damage. Lower concentrations produced slight irritation of the respiratory tract, followed by mild narcosis, weakness, and salivation, but no evidence of eye irritation. However, a single monkey exposed to 1000 ppm for eight 6-hour exposures died. No systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 61
2. Boiling point (760 mm Hg): 101.2 C (214 F)
3. Specific gravity (water = 1): 1.14
4. Vapor density (air = 1 at boiling point of nitromethane): 2.1
5. Melting point: −29 C (−20 F)
6. Vapor pressure at 20 C (68 F): 27.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 9.5
8. Evaporation rate (butyl acetate = 1): 1.39

- **Reactivity**

1. Conditions contributing to instability: Overheating of closed containers may cause detonation.
2. Incompatibilities: Contact with amines, strong acids, and alkalies may sensitize nitromethane so that it will readily explode. Contact with strong oxidizers may cause fires and explosions. Mixtures of nitromethane and hydrocarbons (or other combustible materials) are highly flammable. Contact with some metallic oxides may cause decomposition and development of pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving nitromethane.
4. Special precautions: Liquid nitromethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 35 C (95 F) (closed cup)
2. Autoignition temperature: 418 C (785 F)
3. Flammable limits in air, % by volume: Lower: 7.3; Upper: Data not available
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical

- **Warning properties**

1. Odor Threshold: According to the AIHA *Hygienic Guide*, "the odor is very strong above 100 ppm and irritating at 200 ppm, but cannot be relied on for warning properties." No further explanation is offered. Patty also states, however, that "the odors of nitroparaffins are easily detectable, and concentrations below 200 ppm are disagreeable to most observers. The odor and sensory symptoms are not dependable warning properties."
2. Eye Irritation Level: The *Hygienic Guide* states that "severe eye and respiratory irritation was noted in animals at 500 ppm and above." This is not specifically stated to be the threshold of eye irritation.
3. Evaluation of Warning Properties: Patty states that "the odor and sensory symptoms (of nitroparaffins) are not dependable 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 nitromethane 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 liquid nitromethane.
- Clothing wet with liquid nitromethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitromethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitromethane, the person performing the operation should be informed of nitromethane's hazardous properties.

• Any clothing which becomes wet with liquid nitromethane should be removed immediately and not reworn until the nitromethane is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid nitromethane may contact the eyes.

SANITATION

• Skin that becomes wet with liquid nitromethane should be promptly washed or showered to remove any nitromethane.

• Employees who handle liquid nitromethane should wash their hands thoroughly before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nitromethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in coatings and adhesives on cellulose esters and synthetic resins	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during application by dipping, roller coating, tumbling, knifing, or application of coatings and adhesives	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as an intermediate in synthesis of organic dyes, textiles, surfactants, insecticides, pharmaceuticals, and explosives	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a propellant or fuel additive; use as a reaction-media fluid for Friedel-Crafts reaction; use as a recrystallization solvent; use as a solvent in manufacture of coatings and adhesives on cellulose esters or synthetic resins	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a stabilizer for halogenated alkanes, aerosol formulations, and paste formulations for inks	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 nitromethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid nitromethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid nitromethane 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 nitromethane, 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 nitromethane 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 nitromethane 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 and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an effluent gas cleaning device. Large quantities can be collected, diluted in fuel oil, and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Liquid nitromethane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:
Liquid nitromethane may be disposed of by diluting with fuel oil and atomizing in a suitable combustion chamber equipped with an effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR NITROMETHANE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
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 escape self-contained breathing apparatus.

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

Occupational Health Guideline for 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: $CH_3CH_2CH_2NO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1-nitropropane is 25 parts of 1-nitropropane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 90 milligrams of 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 its recommended Threshold Limit Value for 1-nitropropane from 25 ppm to 15 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1-Nitropropane 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-Nitropropane causes irritation of the eyes and respiratory tract, headache, nausea, vomiting, and diarrhea.

- **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-nitropropane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 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-nitropropane exposure.

—Chronic respiratory disease: 1-Nitropropane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1-nitropropane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: 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-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.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1-Nitropropane vapor is an eye irritant and in animals causes mild respiratory irritation and severe liver damage. Rabbits died from exposure to 5,000 ppm for 3 hours, but 10,000 ppm for 1 hour was not lethal. Effects were conjunctival irritation, lacrimation, slow respiration with some rales, muscular incoordination, ataxia, and weakness. Autopsy of animals exposed to lethal concentrations revealed severe fatty infiltration of the liver and moderate kidney damage. Human volunteers exposed to over 100 ppm noted eye irritation. There are no reports of systemic effects in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

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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1. Molecular weight: 89.1
2. Boiling point (760 mm Hg): 131.6 C (268 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of 1-nitropropane): 3.1
5. Melting point: −108 C (−162 F)
6. Vapor pressure at 20 C (68 F): 7.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.4
8. Evaporation rate (butyl acetate = 1): 0.8

• **Reactivity**

1. Conditions contributing to instability: Overheating in closed containers may cause violent explosion.
2. Incompatibilities: Even though no detonation of 1-nitropropane has been reported, contact with amines, strong acids, and alkalies may cause 1-nitropropane to become unstable. Contact with strong oxidizers may cause fires and explosions. Mixtures of 1-nitropropane and hydrocarbons (or other combustible materials) are highly flammable. Contact with some metal oxides may cause decomposition and development of pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving 1-nitropropane.
4. Special precautions: Liquid 1-nitropropane will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 35.6 C (96 F) (closed cup)
2. Autoignition temperature: 420.6 C (789 F)
3. Flammable limits in air, % by volume: Lower: 2.2; Upper: Data not available
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor (of nitropropane) is detectable at 300 ppm but not at 80 ppm."
2. Eye Irritation Level: Grant states that "tests of nitropropane vapor on human volunteers have established that a sensation of eye irritation is noted at a concentration of 150 ppm in air."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds of nitropropane are not within three times the permissible exposure limit, 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 1-nitropropane 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

• Clothing wet with liquid 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-nitropropane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1-nitropropane, the person performing the operation should be informed of 1-nitropropane's hazardous properties.

• Any clothing which becomes wet with liquid 1-nitropropane should be removed immediately and not reworn until the 1-nitropropane is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid 1-nitropropane may contact the eyes.

SANITATION

• Employees who handle liquid 1-nitropropane 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 1-nitropropane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a thinner and solvent for cellulose compounds, lacquers, and dopes; in vinyl resins for industrial coatings and printing inks; in synthetic finish removers,; and for oil- and spirit-soluble dyes of molded plastics	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an extraction solvent for purification, separation, recrystallization, and recovery for natural and synthetic resins, tars, coating materials, fats, and oils	Local exhaust ventilation; personal protective equipment
Use as a reaction medium in polymer technology, as a catalyst, initiator, and solvent	Local exhaust ventilation; personal protective equipment
Use in organic chemical synthesis for preparation of amines, nitrated alcohols, and acids, and chloronitroparaffins	Local exhaust ventilation; personal protective equipment
Use in manufacture of explosives	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-nitropropane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid 1-nitropropane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid 1-nitropropane soaks 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 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-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 liquid 1-nitropropane 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 and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities can be collected, diluted in fuel oil, and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Liquid 1-nitropropane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Liquid 1-nitropropane may be disposed of by diluting in fuel oil and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR 1-NITROPROPANE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
150 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2300 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 2300 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.

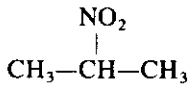
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-NITROPROPANE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about 2-nitropropane 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:** $C_3H_7NO_2$
- **Structure:**



- **Synonyms:** Dimethylnitromethane; isonitropropane; 2-NP
- **Identifiers:** CAS 79-46-9; RTECS TZ5250000; DOT 2608, label required: "Flammable Liquid"
- **Appearance and odor:** Clear, colorless liquid with a fruity odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 89.09
2. Boiling point (at 760 mmHg): 118°-120°C (244°-248°F)
3. Specific gravity (water = 1): 0.992
4. Vapor density (air = 1 at boiling point of 2-nitropropane): 3.07
5. Melting point: -93°C (-135°F)
6. Vapor pressure at 25°C (77°F): 20 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): 1.7
8. Evaporation rate (butyl acetate = 1): 1.62
9. Saturation concentration in air (approximate) at 25°C (77°F): 2.6% (26,000 ppm)
10. Ionization potential: 10.7eV

- **Reactivity**

1. Incompatibilities: Contact with amines, strong acids, alkalies, or strong oxidizers may cause fire and explosion. Contact with some metal oxides may cause decomposition. Mixtures of 2-nitropropane and hydrocarbons are highly flammable.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide and oxides of nitrogen) may be released in a fire involving 2-nitropropane.
3. Caution: Overheating 2-nitropropane in closed container may cause violent explosion. 2-Nitropropane will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: 24°C (75°F) (closed cup)
2. Autoignition temperature: 428°C (802°F)
3. Flammable limits in air, % by volume: Lower, 2.6; upper, 11.0
4. Extinguishant: Dry chemical, foam, or carbon dioxide
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 3

- **Warning properties**

1. Odor threshold: 83 ppm
2. Eye irritation level: 150 ppm
3. 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 2-nitropropane is 25 parts of 2-nitropropane per million parts of air (ppm) [90 milligrams of 2-nitropropane 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 2-nitropropane be controlled and handled as a potential human carcinogen in the workplace; thus, the recommended exposure limit (REL) is that exposure be minimized to the lowest feasible level. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated 2-nitropropane as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 10 ppm (35 mg/m^3) as 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
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for 2-nitropropane

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	25	90
NIOSH REL (Ca)*	Lowest feasible level	
ACGIH TLV® TWA (A2)†	10	35

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

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

• Summary of toxicology

1. *Effects on animals:* In rats, acute inhalation of 2-nitropropane caused progressive weakness, impaired muscular coordination (ataxia), and irregular breathing; in rats, rabbits, and guinea pigs, acute inhalation caused degeneration of the liver (necrosis), pulmonary edema and hemorrhage, selective destruction of brain cells, and vascular epithelial damage in all tissues. Subchronic inhalation of 2-nitropropane by rats produced an increased incidence of liver cancer. Intraperitoneal injection of 2-nitropropane in pregnant rats on days 1 through 15 of gestation caused retarded heart development in unborn fetuses.
2. *Effects on humans:* Acute inhalation exposure of workers to 2-nitropropane has produced toxic hepatitis, gastrointestinal bleeding, pulmonary edema, fatty degeneration and necrosis of the liver, and degeneration of kidney tubules; acute lethal exposure has also occurred. Chronic exposure of workers to 2-nitropropane has been associated with an increased incidence of lymphatic and connective tissue cancers.

• Signs and symptoms of exposure

Short-term (acute): Exposure to 2-nitropropane can cause nausea, vomiting, diarrhea, anorexia, severe headaches, breathing difficulty (dyspnea), impaired muscular coordination, and chest and abdominal pains.

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-nitropropane, 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-nitropropane. 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 disease of the respiratory tract or liver. In addition to the medical interview and physical examination, the means to identify respiratory conditions may include the methods recommended by NIOSH and ATS. The physician should obtain baseline values for tests of liver function.

• 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 2-nitropropane. 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, 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, 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 2-nitropropane may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting 2-nitropropane vapors with Chromosorb 106 tubes followed by desorption with ethyl acetate and analysis by gas chromatography. Direct-reading devices calibrated to measure 2-nitropropane may also be used if available. A detailed sampling and analytical method for 2-nitropropane may be found in the *NIOSH Manual of Analytical Methods* (method number 272).

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 2-nitropropane.

SANITATION

Clothing which is contaminated with 2-nitropropane 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-nitopropane from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-nitropropane'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 2-nitropropane 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 use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 2-nitropropane 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-nitropropane 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-nitropropane

Operations	Controls
During the manufacture and distribution of 2-nitropropane; during maintenance of equipment and storage containers for 2-nitropropane	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture of explosives; during use as a thinner and solvent	Process enclosure, local exhaust ventilation, personal protective equipment
During use in organic chemical synthesis; during use as a propellant in rocket motors	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 2-nitropropane, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-nitropropane 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-nitropropane, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-nitropropane gets on the skin, wash it immediately with soap and water. If 2-nitropropane 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-nitropropane 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-nitropropane, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing 2-nitropropane may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing 2-nitropropane 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 2-nitropropane

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 appropriate escape-type self-contained breathing apparatus

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

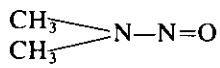
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR N-NITROSODIMETHYLAMINE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about N-nitrosodimethylamine 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:** $C_2H_6N_2O$
- **Structure:**



- **Synonyms:** Dimethylnitrosamine; N,N-dimethylnitrosamine; dimethylnitrosoamine; DMN; DMNA; N-methyl-N-nitrosomethanamine; NDMA; nitrosodimethylamine
- **Identifiers:** CAS 62-75-9; RTECS IQ0525000; DOT not assigned
- **Appearance and odor:** Yellow liquid of low viscosity

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 74.10
2. Boiling point (at 760 mmHg): 152°C (305.6°F)
3. Specific gravity (water = 1): 1.005
4. Vapor density (air = 1 at boiling point of N-nitrosodimethylamine): 2.56
5. Soluble in water

- **Reactivity**

1. Incompatibilities: Ultraviolet light; strong oxidizing agents
2. Hazardous decomposition products: Toxic vapors and gases (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving N-nitrosodimethylamine.
3. Caution: Store in dark bottles.

- **Flammability**

Extinguishant: Dry chemical, alcohol foam, or 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 N-nitrosodimethylamine; however, the OSHA standard requires implementation of stringent controls wherever N-nitrosodimethylamine or solid or liquid mixtures containing at least 0.1% by weight or volume of N-nitrosodimethylamine 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 1910.1016, N-Nitrosodimethylamine. The National Institute for Occupational Safety and Health (NIOSH) concurs with the OSHA standard. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated N-nitrosodimethylamine as an A2 substance (suspected human carcinogen) without having sufficient evidence to assign a threshold limit value (TLV®) (Skin). The notation "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

N-nitrosodimethylamine may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

- **Summary of toxicology**

1. *Effects on animals:* Acute intraperitoneal injection of N-nitrosodimethylamine in rats produced cancer of the nasal cavity. In multiple species of animals, subchronic or chronic exposure via several routes of administration produced cancers of the liver, kidneys, or lungs. Intravenous or interplacental injections of N-nitrosodimethylamine in rats caused increased embryolethality and fetal mortality.
2. *Effects on humans:* Acute exposure of laboratory workers to N-nitrosodimethylamine has caused inflammation, degeneration, cirrhosis, and dysfunction of the liver and death.

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• **Signs and symptoms of exposure**

Short-term (acute): Exposure to N-nitrosodimethylamine can cause vomiting, abdominal cramps, diarrhea, headache, fever, and jaundice.

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-nitrosodimethylamine, 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, 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 N-nitrosodimethylamine. 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 N-nitrosodimethylamine. 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 of and physiologic function of the liver, kidneys, 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 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 N-nitrosodimethylamine may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

• **Method**

Sampling and analysis may be performed by collecting N-nitrosodimethylamine vapors with Tenax GC in short glass tubes followed by desorption by heating and purging with helium, separation by capillary gas-liquid chromatography, and analysis by mass spectrometry. Direct-reading devices calibrated to measure N-nitrosodimethylamine may also be used if applicable. A detailed sampling and analytical method for N-nitrosodimethylamine may be found in the *NIOSH Manual of Analytical Methods* (method number 252).

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 N-nitrosodimethylamine 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 N-nitrosodimethylamine 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 N-nitrosodimethylamine 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 N-nitrosodimethylamine from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of N-nitrosodimethylamine'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 N-nitrosodimethylamine 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 1910.1016:

Areas where N-nitrosodimethylamine 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 are 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 N-nitrosodimethylamine, 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 N-nitrosodimethylamine which are not in an isolated system, laboratory-type hood, or other system affording equivalent protection against the entry of N-nitrosodimethylamine into regulated areas, nonregulated areas, or the external environment are prohibited.

In operations involving "laboratory-type hoods" or in locations where N-nitrosodimethylamine 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 N-nitrosodimethylamine 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 N-nitrosodimethylamine from materials, equipment, and decontamination facility.

COMMON OPERATIONS AND CONTROLS

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

EMERGENCY FIRST AID PROCEDURES

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

Table 1.—Operations and methods of control for N-nitrosodimethylamine

Operations	Controls
During use in the production of rocket fuel; during use as a solvent in the fibers and plastics industries, as an oxidant, and as an additive in lubricants	Process enclosure, restricted access, local exhaust ventilation, personal protective equipment, good housekeeping and personal hygiene practices, substitution with less toxic substance

cy procedures. If a worker has contact with N-nitrosodimethylamine, 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 N-nitrosodimethylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

If N-nitrosodimethylamine 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-nitrosodimethylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If N-nitrosodimethylamine gets on the skin, wash it immediately with soap and water. If N-nitrosodimethylamine 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 N-nitrosodimethylamine is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. For small quantities liquids containing N-nitrosodimethylamine, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing N-nitrosodimethylamine may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. Liquids containing N-nitrosodimethylamine 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 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 N-nitrosodimethylamine

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 Nitrotoluene

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: Ortho: $2\text{-}NO_2C_6H_4CH_3$; Meta: $3\text{-}NO_2C_6H_4CH_3$; Para: $4\text{-}NO_2C_6H_4CH_3$

• Synonyms: Orthonitrotoluene; o-nitrotoluol; metanitrotoluene; m-nitrotoluol; paranitrotoluene; p-nitrotoluol

• Appearance and odor: Ortho: Yellow liquid or solid with a weak aromatic odor; Meta: Yellow liquid or solid with a weak aromatic odor; Para: Pale yellow solid with a weak aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrotoluene is 5 parts of nitrotoluene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 30 milligrams of nitrotoluene per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for nitrotoluene from 5 ppm to 2 ppm with a skin notation.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Nitrotoluene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It is readily absorbed through the skin.

• **Effects of overexposure**

Nitrotoluene may affect the ability of the blood to carry oxygen. This may cause a bluish discoloration of the skin, irritability, drowsiness, nausea, rapid pulse, headache, weakness, shortness of breath, and unconsciousness.

• **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 nitrotoluene.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrotoluene 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, nervous system, gastrointestinal system, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Nitrotoluene has been shown to cause methemoglobinemia. Persons with blood disorders may be at increased risk from exposure. 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. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

• **Summary of toxicology**

Nitrotoluene, whether absorbed as vapor by inhalation or as liquid through the skin, has a potential for producing methemoglobin and subsequent anoxia. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. The onset of symptoms of methemoglobinemia is insidious and may be delayed up to 4 hours; headache is commonly 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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first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis occurs when the methemoglobin concentration is 15% or more. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and is usually recognized by fellow workers. Until the methemoglobin concentration approaches approximately 40%, the individual usually feels well, has no complaints, and will insist that nothing is wrong. At methemoglobin concentrations of over 40%, there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 137.1
  2. Boiling point (760 mm Hg): Ortho: 222 C (432 F); Meta: 232 C (450 F); Para: 238 C (460 F)
  3. Specific gravity (water = 1): Ortho: 1.16; Meta: 1.16; Para: 1.3
  4. Vapor density (air = 1 at boiling point of nitrotoluene): 4.7
  5. Melting point: Ortho: −4 C (25 F); Meta: 16 C (61 F); Para: 52 C (126 F)
  6. Vapor pressure at 20 C (68 F): Ortho and Meta: 0.15 mm Hg; Para: 0.12 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 0.06; Meta: 0.05; Para: 0.004
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers or sulfuric acid 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 nitrotoluene.
  4. Special precautions: Nitrotoluene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Ortho: 106 C (223 F) (closed cup); Meta: 101 C (214 F); Para: 106 C (223 F)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: Ortho: 2.2 (calculated); Meta and para: 1.6 (calculated)
  4. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**
  1. Odor Threshold: Information is not available.
  2. Eye Irritation Level: Nitrotoluene is not known to be an eye irritant.
  3. Evaluation of Warning Properties: 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 a silica gel adsorption tube with subsequent desorption using methanol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrotoluene may be used. An analytical method for nitrotoluene 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 or liquid nitrotoluene.
- Non-impervious clothing which becomes contaminated with nitrotoluene should be removed promptly and not reworn until the nitrotoluene is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid or liquid nitrotoluene may contact the eyes.

SANITATION

• Skin that becomes contaminated with nitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any nitrotoluene.
• Eating and smoking should not be permitted in areas where solid nitrotoluene is handled, processed, or stored.
• Employees who handle solid or liquid nitrotoluene 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 nitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of toluidines for the production of dyes, intermediates for vulcanization accelerators, gasoline inhibitors, and flotation agents; use as an analytical reagent	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in the manufacture of dinitrotoluenes for production of explosives; manufacture of nitrotoluene-sulfonic acids for production of azo and stilbene dyes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for intermediates of dyes, sun screening agents, and fuchsin— a red dye used in textile and leather industries	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 solid or liquid nitrotoluene 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 solid or liquid nitrotoluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid nitrotoluene penetrates 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 nitrotoluene, 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 nitrotoluene 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 nitrotoluene is spilled or leaked, the following steps should be taken:
1. Ventilate area of spill or leak.
2. For small quantities of liquid nitrotoluene, absorb on paper towels. For small quantities of solid nitrotoluene, sweep onto paper or other suitable material. Remove to a safe place (such as a fume hood) and burn the paper. Large quantities of liquid nitrotoluene can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Large quantities of solid nitrotoluene can 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:
Nitrotoluene may be disposed of:
1. For liquid nitrotoluene, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing liquid nitrotoluene in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By making packages of solid nitrotoluene in paper or

other suitable material or by dissolving in a flammable solvent (such as alcohol) and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR NITROTOLUENE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor or Particulate Concentration	
50 ppm or 280 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
200 ppm or 1120 mg/m³ 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 200 ppm or 1120 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. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Nitrotoluene

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: Ortho: $2\text{-}NO_2C_6H_4CH_3$; Meta: $3\text{-}NO_2C_6H_4CH_3$; Para: $4\text{-}NO_2C_6H_4CH_3$

• Synonyms: Orthonitrotoluene; o-nitrotoluol; metanitrotoluene; m-nitrotoluol; paranitrotoluene; p-nitrotoluol

• Appearance and odor: Ortho: Yellow liquid or solid with a weak aromatic odor; Meta: Yellow liquid or solid with a weak aromatic odor; Para: Pale yellow solid with a weak aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrotoluene is 5 parts of nitrotoluene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 30 milligrams of nitrotoluene per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for nitrotoluene from 5 ppm to 2 ppm with a skin notation.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Nitrotoluene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It is readily absorbed through the skin.

• **Effects of overexposure**

Nitrotoluene may affect the ability of the blood to carry oxygen. This may cause a bluish discoloration of the skin, irritability, drowsiness, nausea, rapid pulse, headache, weakness, shortness of breath, and unconsciousness.

• **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 nitrotoluene.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrotoluene 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, nervous system, gastrointestinal system, and cardiovascular system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Nitrotoluene has been shown to cause methemoglobinemia. Persons with blood disorders may be at increased risk from exposure. 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. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

• **Summary of toxicology**

Nitrotoluene, whether absorbed as vapor by inhalation or as liquid through the skin, has a potential for producing methemoglobin and subsequent anoxia. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. The onset of symptoms of methemoglobinemia is insidious and may be delayed up to 4 hours; headache is commonly 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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first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis occurs when the methemoglobin concentration is 15% or more. Cyanosis develops early in the course of intoxication, first in the lips, the nose, and the ear lobes, and is usually recognized by fellow workers. Until the methemoglobin concentration approaches approximately 40%, the individual usually feels well, has no complaints, and will insist that nothing is wrong. At methemoglobin concentrations of over 40%, there usually is weakness and dizziness; at up to 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 137.1
  2. Boiling point (760 mm Hg): Ortho: 222 C (432 F); Meta: 232 C (450 F); Para: 238 C (460 F)
  3. Specific gravity (water = 1): Ortho: 1.16; Meta: 1.16; Para: 1.3
  4. Vapor density (air = 1 at boiling point of nitrotoluene): 4.7
  5. Melting point: Ortho: −4 C (25 F); Meta: 16 C (61 F); Para: 52 C (126 F)
  6. Vapor pressure at 20 C (68 F): Ortho and Meta: 0.15 mm Hg; Para: 0.12 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 0.06; Meta: 0.05; Para: 0.004
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers or sulfuric acid 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 nitrotoluene.
  4. Special precautions: Nitrotoluene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Ortho: 106 C (223 F) (closed cup); Meta: 101 C (214 F); Para: 106 C (223 F)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: Ortho: 2.2 (calculated); Meta and para: 1.6 (calculated)
  4. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**
  1. Odor Threshold: Information is not available.
  2. Eye Irritation Level: Nitrotoluene is not known to be an eye irritant.
  3. Evaluation of Warning Properties: 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 a silica gel adsorption tube with subsequent desorption using methanol and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrotoluene may be used. An analytical method for nitrotoluene 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 or liquid nitrotoluene.
- Non-impervious clothing which becomes contaminated with nitrotoluene should be removed promptly and not reworn until the nitrotoluene is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid or liquid nitrotoluene may contact the eyes.

SANITATION

• Skin that becomes contaminated with nitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any nitrotoluene.
• Eating and smoking should not be permitted in areas where solid nitrotoluene is handled, processed, or stored.
• Employees who handle solid or liquid nitrotoluene 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 nitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of toluidines for the production of dyes, intermediates for vulcanization accelerators, gasoline inhibitors, and flotation agents; use as an analytical reagent	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in the manufacture of dinitrotoluenes for production of explosives; manufacture of nitrotoluene-sulfonic acids for production of azo and stilbene dyes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for intermediates of dyes, sun screening agents, and fuchsin— a red dye used in textile and leather industries	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 solid or liquid nitrotoluene 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 solid or liquid nitrotoluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid nitrotoluene penetrates 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 nitrotoluene, 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 nitrotoluene 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 nitrotoluene is spilled or leaked, the following steps should be taken:
1. Ventilate area of spill or leak.
2. For small quantities of liquid nitrotoluene, absorb on paper towels. For small quantities of solid nitrotoluene, sweep onto paper or other suitable material. Remove to a safe place (such as a fume hood) and burn the paper. Large quantities of liquid nitrotoluene can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Large quantities of solid nitrotoluene can 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:
Nitrotoluene may be disposed of:
1. For liquid nitrotoluene, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing liquid nitrotoluene in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By making packages of solid nitrotoluene in paper or

other suitable material or by dissolving in a flammable solvent (such as alcohol) and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Nitrotoluene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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  7. Solubility in water, g/100 g water at 20 C (68 F): Ortho: 0.06; Meta: 0.05; Para: 0.004
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers or sulfuric acid 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 nitrotoluene.
  4. Special precautions: Nitrotoluene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Ortho: 106 C (223 F) (closed cup); Meta: 101 C (214 F); Para: 106 C (223 F)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Lower: Ortho: 2.2 (calculated); Meta and para: 1.6 (calculated)
  4. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**
  1. Odor Threshold: Information is not available.
  2. Eye Irritation Level: Nitrotoluene is not known to be an eye irritant.
  3. Evaluation of Warning Properties: 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).

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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 nitrotoluene.
- Non-impervious clothing which becomes contaminated with nitrotoluene should be removed promptly and not reworn until the nitrotoluene is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid or liquid nitrotoluene may contact the eyes.

SANITATION

• Skin that becomes contaminated with nitrotoluene should be promptly washed or showered with soap or mild detergent and water to remove any nitrotoluene.
• Eating and smoking should not be permitted in areas where solid nitrotoluene is handled, processed, or stored.
• Employees who handle solid or liquid nitrotoluene 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 nitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of toluidines for the production of dyes, intermediates for vulcanization accelerators, gasoline inhibitors, and flotation agents; use as an analytical reagent	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in the manufacture of dinitrotoluenes for production of explosives; manufacture of nitrotoluene-sulfonic acids for production of azo and stilbene dyes	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for intermediates of dyes, sun screening agents, and fuchsin— a red dye used in textile and leather industries	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 solid or liquid nitrotoluene 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 solid or liquid nitrotoluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid nitrotoluene penetrates 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 nitrotoluene, 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 nitrotoluene 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 nitrotoluene is spilled or leaked, the following steps should be taken:
1. Ventilate area of spill or leak.
2. For small quantities of liquid nitrotoluene, absorb on paper towels. For small quantities of solid nitrotoluene, sweep onto paper or other suitable material. Remove to a safe place (such as a fume hood) and burn the paper. Large quantities of liquid nitrotoluene can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Large quantities of solid nitrotoluene can 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:
Nitrotoluene may be disposed of:
1. For liquid nitrotoluene, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing liquid nitrotoluene in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By making packages of solid nitrotoluene in paper or

other suitable material or by dissolving in a flammable solvent (such as alcohol) and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR NITROTOLUENE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor or Particulate Concentration	
50 ppm or 280 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
200 ppm or 1120 mg/m³ 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 200 ppm or 1120 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. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Octachloronaphthalene

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: $C_{10}Cl_8$
- Synonyms: Halowax 1051
- Appearance and odor: Pale, yellow solid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for octachloronaphthalene is 0.1 milligram of octachloronaphthalene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Octachloronaphthalene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Overexposure to octachloronaphthalene may cause an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, yellow jaundice, and possibly 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 octachloronaphthalene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to octachloronaphthalene 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: Octachloronaphthalene may cause liver damage. A profile of liver function should be performed by using 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**

Octachloronaphthalene may be regarded, mainly by analogy to the lower chlorinated naphthalenes such as the penta- and hexachlor derivatives, as probably toxic to the liver and the skin. There is no information on the effects of inhalation of vapor or dust on man. Ingestion experiments on cattle suggest that the octachlor is more toxic but less readily absorbed than the hexachlor derivative. Exposure of workers by inhalation or skin absorption to mixtures of chlorinated naphthalenes with a lower chlorine content has caused a severe acne-form dermatitis termed chloracne, as well as serious liver injury.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 403.7
2. Boiling point (760 mm Hg): 410 C (770 F) (approximately)
3. Specific gravity (water = 1): 2.0
4. Vapor density (air = 1 at boiling point of octachloronaphthalene): 13.9

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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5. Melting point: 185 C (365 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: 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 and toxic chloride fumes) may be released in a fire involving octachloronaphthalene.

4. Special precautions: None

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: No quantitative information is available.

2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "eye injury has not proved to be troublesome with the chloronaphthalenes."

3. Evaluation of Warning Properties: There are no quantitative data relating warning properties to air concentrations of octachloronaphthalene; therefore, this substance is treated as a material with poor warning properties. The concentration of octachloronaphthalene in saturated air at 20 C could present a significant exposure relative to the permissible 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 octachloronaphthalene on a filter, followed by extraction with hexane, and gas chromatographic analysis. An analytical method for octachloronaphthalene 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 molten octachloronaphthalene.

• 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 octachloronaphthalene or liquids containing octachloronaphthalene.

• 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 octachloronaphthalene vapors from the heated material.

• If employees' clothing may have become contaminated with solid octachloronaphthalene, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with molten octachloronaphthalene should be removed immediately and not reworn until the octachloronaphthalene is removed from the clothing.

• Non-impervious clothing which becomes contaminated with solid octachloronaphthalene or liquids containing octachloronaphthalene should be removed promptly and not reworn until the octachloronaphthalene is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten octachloronaphthalene contacting the eyes.

• Employees should be provided with and required to use splash-proof safety goggles where solid octachloronaphthalene or liquids containing octachloronaphthalene may contact the eyes.

SANITATION

• Workers subject to skin contact with octachloronaphthalene should wash with soap or mild detergent and water any areas of the body which may have contacted octachloronaphthalene at the end of each work day.

• Skin that becomes contaminated with octachloronaphthalene should be promptly washed or showered with soap or mild detergent and water to remove any octachloronaphthalene.

• Eating and smoking should not be permitted in areas where solid octachloronaphthalene is handled, processed, or stored.

• Employees who handle solid octachloronaphthalene or liquids containing octachloronaphthalene 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 octachloronaphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture of electric equipment as an insulating material; pouring molten solvent or finely ground solid materials; dipping; peeling and covering insulated cable with fabric	Local exhaust ventilation; general dilution with intake and exhaust fans; personal protective equipment
Liberation from use of electrical equipment insulated with octachloronaphthalene/ pentachloro-naphthalene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an inert compound of resins or polymers for coating or impregnating textiles, wood, and paper to impart flame resistance, water proofness, and fungicidal and insecticidal properties	Process enclosure; local exhaust ventilation; general dilution with intake and exhaust fans; personal protective equipment
Use as an additive for cutting oil in various operations performed on metals	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an additive to special lubricants in crankcase oil, lubricants for farm machinery, and extreme-pressure lubricants	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 solid octachloronaphthalene or liquids containing octachloronaphthalene 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. If molten octachloronaphthalene gets into the eyes, immediately flush the eyes with large amounts of water to remove heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If non-impervious clothing becomes contaminated with octachloronaphthalene, remove and clean the clothing before wearing it again. If non-impervious clothing becomes heavily contaminated, it should be destroyed. If solid octachloronaphthalene or liquids containing octachloronaphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If skin irritation persists after washing, get medical attention. If molten octachloronaphthalene gets on the skin or non-impervious clothing, immediately flush the affected area with large amounts of water to remove heat. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of octachloronaphthalene, 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 octachloronaphthalene 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 octachloronaphthalene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing octachloronaphthalene should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Octachloronaphthalene may be disposed of in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Octachloronaphthalene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• 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 OCTACHLORONAPHTHALENE

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate 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.
100 mg/m³ or less	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.
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 Octane

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_8H_{18}
- Synonyms: Normal octane
- Appearance and odor: Colorless liquid with a gasoline-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for octane is 500 parts of octane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2350 milligrams of octane per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 75 ppm (350 mg/m³) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 385 ppm (1800 mg/m³) averaged over a 15-minute period. The NIOSH Criteria Document for Alkanes should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Octane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to octane may cause irritation of the eyes, nose, and skin, and drowsiness. Exposure to higher air concentrations may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure 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 octane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to octane 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems and the skin should be stressed.

—Skin disease: Octane is a skin 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 octane 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 octane 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 octane might cause exacerbation of symptoms due to its irritant properties.

*2. Periodic Medical Examination:*The aforementioned medical examinations should be performed on an annual basis.

- **Summary of toxicology**

Octane vapor is a mild narcotic and mucous membrane irritant. Mice exposed at concentrations of 6600 to 13,700 ppm demonstrated signs of narcosis in 30 to 90 minutes. The narcotic concentration is approximately 8000 ppm, while the fatal concentration for animals is

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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near 13,500 ppm. Repeated or prolonged skin contact with the liquid results in drying and cracking skin due to defatting action. No chronic systemic effects have been reported in humans. Aspiration may cause chemical pneumonia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 114.2
  2. Boiling point (760 mm Hg): 126 C (258 F)
  3. Specific gravity (water = 1): 0.7
  4. Vapor density (air = 1 at boiling point of octane): 3.9
  5. Melting point: −56.7 C (−70 F)
  6. Vapor pressure at 20 C (68 F): 11 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.04 (approximately)
  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 octane.
  4. Special precautions: Octane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 13.3 C (56 F) (closed cup)
  2. Autoignition temperature: 220 C (428 F)
  3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 6.5
  4. Extinguishant: Foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Summer and May both report an odor threshold of 150 ppm for octane.
  2. Eye Irritation Level: According to the *Handbook of Organic Industrial Solvents*, "irritation occurs as exposure exceeds threshold limit."
  3. Evaluation of Warning Properties: Because of its low thresholds of odor and irritation, octane 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 octane. 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 octane 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 octane may be used. An analytical method for octane 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 octane.
- Any clothing which becomes wet with liquid octane should be removed immediately and not reworn until the octane is removed from the clothing.
- Clothing wet with liquid octane should be placed in closed containers for storage until it can be discarded or

until provision is made for the removal of octane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the octane, the person performing the operation should be informed of octane's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where liquid octane may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to octane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes wet with liquid octane should be promptly washed or showered with soap or mild detergent and water to remove any octane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to octane may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of gasoline, rocket fuel, and of fuel cells, and in combustion studies	General dilution ventilation; local exhaust ventilation
Use as an industrial solvent as lacquer diluent, phosphate manufacture, and preparation of liquid soaps and detergents	General dilution ventilation; local exhaust ventilation
Use in azeotropic mixtures for printing ink manufacture, and separation distillation	General dilution ventilation; local exhaust ventilation
Use as an additive and solvent in polymer manufacture	General dilution ventilation; local exhaust ventilation
Use in manufacture of benzene, toluene, and xylene aromatics	Process enclosure; local exhaust ventilation; personal protective equipment
Use in laboratory procedures and studies	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a blowing agent for foam rubber used in rocket propellants	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 octane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If octane gets on the skin, promptly wash the contaminated skin using soap or mild detergent. If octane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of octane, 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 octane 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 octane 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. Octane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Octane may be disposed of by atomizing in a suitable combustion chamber.

REFERENCES

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RESPIRATORY PROTECTION FOR OCTANE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator. Any self-contained breathing apparatus.
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 Health Guideline for Mineral Oil Mist

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_nH_{2n+2} where n = 16 and up
- Synonyms: The mist of petroleum-based: white mineral oil; cutting oils; heat-treating oils; hydraulic oils; cable oil; transformer oil; lubricating oils; drawing oils
- Appearance and odor: Mist with an odor like burned lube oil generated from petroleum-base or white mineral petroleum oil.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for mineral oil mist is 5 milligrams of mineral oil mist per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Mineral oil mist can affect the body if it is inhaled.

- **Effects of overexposure**

Inhalation of mineral oil mist may cause adverse respiratory effects.

- **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 mineral oil mist.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to mineral oil mist 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 mineral oil mist exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of mineral oil mist might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Prolonged exposure to mineral oil mist may cause a dermatitis. 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**

Inhalation of mineral oil mist in high concentrations may cause pulmonary effects, although this has rarely been reported. A single case of lipoid pneumonitis suspected to have been caused by exposure to very high concentrations of oil mist was reported in 1950; this occurred in a cash register serviceman, whose heavy exposure occurred over 17 years of employment; no other cases have been recorded. Experimental animal exposure studies to white mineral oil mist (untreated, and with no additions) for repeated daily 6-hour exposures for 1 year at 5 mg/m^3 were entirely negative in all criteria used for measuring response. A similar study at 100 mg/m^3 resulted in some slight changes in some but not all species exposed; no histologic changes of significance were noted. Exposure to oil mist did not appear to accelerate the production of lung tumors in a lung-tumor-susceptible strain of mice. A second parallel study of sulfurized, solvent-extracted naphthenic-base oil to which animals were exposed daily at 50 mg/m^3 for 18 months failed to reveal a single animal with any sort of injury or indisposition as a result of the oil mist inhalation. A review of exposures to mineral oil mist averaging 15 mg/m^3 (but often higher) in several industries disclosed a striking lack of reported cases of illness related to these exposures. A study of oil mist

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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exposures in machine shops, at mean concentrations of 3.7 mg/m³ and maximum of 110 mg/m³, showed no increase in respiratory symptoms or decrement in respiratory performance attributable to oil mist inhalation among men employed for many years. There is no evidence to suggest any relation between in- halation of oil mist and lung cancer. On the other hand, there are some reported cases of skin cancer from contact with certain oils. Contact with liquid oils may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: Not pertinent
  2. Boiling point (760 mm Hg): 360 C (680 F)
  3. Specific gravity (water = 1): 0.8 – 0.9
  4. Vapor density (air = 1 at boiling point of mineral oil mist): Not applicable
  5. Melting point: Very low
  6. Vapor pressure at 20 C (68 F): Very low
  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: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Flash point: 135 C (275 F) (closed cup)
  2. Autoignition temperature: 260 – 371 C (500 – 700 F)
  3. Flammable limits in air, % by volume: Not applicable
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**

Mineral oil mist 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 mineral oil mist on a filter, followed by treatment with chloroform and analysis by fluorescence spectrophotometry. An analytical method for mineral oil mist 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 repeated or prolonged skin contact with liquid mineral oil.
- Non-impervious clothing which becomes wet with liquid mineral oil should be removed promptly and not reworn until the mineral oil mist is removed from the clothing.

SANITATION

- Skin that becomes wet with liquid mineral oil should be promptly washed or showered with soap or mild detergent and water to remove any mineral oil mist.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to mineral oil mist may occur and control methods which may be effective in each case:

Operation	Controls
Use as a coolant or quenching agent in machine shop operations and metal fabrication; during coating and cleaning in foundry operations	Process enclosure; local exhaust ventilation; general mechanical ventilation
Use in steel rolling operations; use in lubricating and cleaning of machinery	Process enclosure; local exhaust ventilation; general mechanical ventilation
Use in pressroom operations in printing	Mist suppression; local exhaust ventilation; general mechanical ventilation
Use in mine drilling operations	Process enclosure; local exhaust ventilation; general mechanical ventilation
Use as an insecticide	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.

• **Skin Exposure**

If skin becomes wet with mineral oil mist, wash the contaminated skin using soap or mild detergent and water. If mineral oil mist penetrates through the clothing, remove the clothing and wash the skin using soap or mild detergent and water.

• **Breathing**

If a person breathes in large amounts of mineral oil mist, move the exposed person to fresh air at once.

SPILL, LEAK, 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 mineral oil mist is released in hazardous concentrations, ventilate area of release to disperse the mist.

• If mineral oil mist 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.

• Waste disposal methods:

Mineral oil mist 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 MINERAL OIL MIST

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
25 mg/m³ or less	Any mist respirator, except single-use.
50 mg/m³ or less	Any 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.
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. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
2,500 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 2,500 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 Health Guideline for Osmium Tetroxide

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: OsO_4
- Synonyms: Osmic acid
- Appearance and odor: Colorless to pale yellow solid with a sharp, choking, chlorine-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for osmium tetroxide is 0.002 milligrams of osmium tetroxide 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 osmium tetroxide a Threshold Limit Value of 0.0002 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Osmium tetroxide 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 osmium tetroxide may cause severe eye damage accompanied by irritation with tearing. This may occur several hours after exposure has ceased. After exposure, halos may be seen around lights. Exposure to osmium tetroxide may also cause severe irritation of the nose, throat, and bronchial tubes with cough, wheezing, shortness of breath, and pneumonia. In addition, exposure to this chemical may also cause skin burns, skin rash, skin discoloration, and kidney 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 osmium tetroxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to osmium tetroxide 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 osmium tetroxide exposure.

—Eye disease: Osmium tetroxide is an eye irritant and in workers has caused symptoms and signs of keratitis epithelia with corneal edema. Persons with pre-existing eye 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 osmium tetroxide might cause exacerbation of symptoms due to its irritant properties.

—Kidney disease: Osmium tetroxide causes mild kidney damage in animals. Persons with pre-existing kidney disease may be more susceptible to the effects of this agent.

—Skin disease: Osmium tetroxide 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**

Osmium tetroxide as dust or vapor is a severe irritant of the eyes and respiratory tract. Rabbits exposed for 30 minutes to vapor at estimated concentrations of 130 mg/m^3 developed irritation of mucous membranes and labored breathing; at autopsy there was bronchopneumonia, as well as slight kidney damage. A laboratory investigator exposed to a high concentration of vapor experienced a sensation of chest constriction and diffi-

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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culty in breathing. Irritation of the eyes is usually the first symptom of exposure to low concentrations of the vapor; lacrimation, a gritty feeling in the eyes, and the appearance of rings around lights are frequently reported; in most cases, recovery occurs within a few days. Workers exposed to fume concentrations up to 0.6 mg/m^3 developed lacrimation, visual disturbances, and, in some cases, frontal headache, conjunctivitis, and cough. Application of a drop of 1% solution of osmium tetroxide to a rabbit eye caused severe corneal damage; there was permanent opacity and superficial vascularization. Osmium compounds have a caustic action on the skin resulting in eczema and dermatitis. Osmium tetroxide is a very irritating material to the skin due to its ability to precipitate protein.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 2.54
2. Boiling point (760 mm Hg): 130 C (266 F) (sublimes well below boiling point)
3. Specific gravity (water = 1): 4.9
4. Vapor density (air = 1 at boiling point of osmium tetroxide): 8.8
5. Melting point: 42 C (108 F)
6. Vapor pressure at 20 C (68 F): 7 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 7
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with hydrochloric acid will cause formation of poisonous chlorine gas. Contact with easily oxidized organic materials may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: According to Hunter, osmium tetroxide has an irritating odor, but no quantitative information is available concerning the odor threshold.

2. Eye Irritation Level: Grant states that "the eyes are particularly susceptible to injury by vapors of osmium tetroxide. With sufficient concentrations a sensation of irritation with lacrimation and sensation of foreign body is induced immediately. This may be accompanied by irritation of the nose and throat . . . . Concentrations of vapor which do not cause immediate sensation of irritation have an insidious cumulative action with a latent period before the onset of smarting and lacrimation, which may be delayed from 1 to several hours after start of exposure. In either case the symptoms and signs are those of keratitis epithelialis with corneal epithelial edema . . . . No permanent effect has been noted, even when several episodes of keratitis epithelialis have been experienced." Grant later states, however, that application of a drop of 1% solution of osmium tetroxide on rabbit eyes resulted in "moderate permanent opacity."

3. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of osmium tetroxide, and since this is such an extremely toxic substance, it should be 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 osmium tetroxide 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 skin contact with osmium tetroxide or liquids containing osmium tetroxide, where skin contact may occur.
- If employees' clothing may have become contaminated with solid osmium tetroxide, employees should

change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with osmium tetroxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of osmium tetroxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the osmium tetroxide, the person performing the operation should be informed of osmium tetroxide's hazardous properties.

• Non-impervious clothing which becomes contaminated with osmium tetroxide should be removed promptly and not reworn until the osmium tetroxide 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 solid or liquid osmium tetroxide or liquids containing osmium tetroxide contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to solid or liquid osmium tetroxide or liquids containing osmium tetroxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with osmium tetroxide should be promptly washed or showered to remove any osmium tetroxide.

• Eating and smoking should not be permitted in areas where solid or liquid osmium tetroxide or liquids containing osmium tetroxide are handled, processed, or stored.

• Employees who handle solid or liquid osmium tetroxide or liquids containing osmium tetroxide 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 osmium tetroxide may occur and control methods which may be effective in each case:

Operation	Controls
By-product during refining and processing of osmiridium and other platinum metal ores; during production of alloys; during casting and annealing operations in manufacture of specialty metal products	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an intermediate for separation of metals and ores of osmium from platinum; use as a catalyst for oxidizing agent in organic synthesis; use as a staining and fixing agent in pathological and histological analysis; use 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 osmium tetroxide 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 solid or liquid osmium tetroxide or liquids containing osmium tetroxide get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solid or liquid osmium tetroxide or liquids containing osmium tetroxide 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 osmium tetroxide, 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 osmium tetroxide 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 solid or liquid osmium tetroxide or liquids containing osmium tetroxide are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing osmium tetroxide should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Osmium tetroxide may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Osmium Tetroxide," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR OSMIUM TETROXIDE

Condition	Minimum Respiratory Protection* Required Above 0.002 mg/m³
Particulate and Vapor Concentration	
0.1 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1 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 1 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 with a high efficiency filter providing protection against osmium tetroxide vapors and particulates. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Oxalic Acid

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: $HOOCCOOH\text{-}2H_2O$
- Synonyms: Oxalic acid dihydrate; ethanedioic acid
- Appearance and odor: Colorless, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for oxalic acid is 1 milligram of oxalic acid per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Oxalic acid can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may slowly enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Exposure to either solid or liquid oxalic acid can cause severe burns of the skin, eyes, and linings of the respiratory tract. A number of deaths have occurred from swallowing oxalic acid. The symptoms appear rapidly and include shock, collapse, and convulsive seizures. Such cases may also have marked kidney damage.

2. Long-term Exposure: Prolonged or repeated skin contact with oxalic acid solutions may cause pain and discoloration of the fingers. This may go on to gangrene.

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 oxalic acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to oxalic acid 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 oxalic acid exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of oxalic acid might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Oxalic acid is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Oxalic acid may cause kidney damage. Special consideration should be given to exposing those with impaired renal function.

—Eye disease: Oxalic acid is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems 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**

Oxalic acid as a dust or in solution irritates the eyes, mucous membranes, and skin. There is little reported information on industrial exposures, although chronic inflammation of the upper respiratory tract has been described in a worker exposed to hot vapors (probably an aerosol) arising from oxalic acid. Solutions are irritating to the skin after prolonged exposure and may cause localized pain, with cyanosis of the fingers and even gangrenous changes. Splashes in the eye produce epithelial damage from which recovery is usually prompt. Fatalities have been reported following ingestion of as little as 5 g; the onset of symptoms is rapid, including those of shock, collapse, and convulsions;

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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there may be marked renal damage, with deposition of calcium oxalate in the lumen of the renal tubules.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 126.1
  2. Boiling point (760 mm Hg): Sublimes at 149– 160 C (300– 320 F) with partial decomposition
  3. Specific gravity (water = 1): 1.5
  4. Vapor density (air = 1 at boiling point of oxalic acid): 4.3
  5. Melting point: 101.5 C (215 F)
  6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 10
  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. Contact with silver compounds may form explosive silver oxalate salt.
  3. Hazardous decomposition products: Toxic gases and vapors (such as formic acid and carbon monoxide) may be released in a fire involving oxalic acid.
  4. Special precautions: None
- **Flammability**
  1. Flash point: None by standard tests
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Water spray, dry chemical, or carbon dioxide
- **Warning properties**

Grant reports that "oxalic acid, a crystalline solid, readily soluble in water, has caused burns of the human eye in a few instances when solutions accidentally came in contact with the eye. The injury has been epithelial, and recovery has been prompt, the epithelium regenerating usually within two days . . . ." Grant observed that the application of a 5% solution for 30 seconds to rabbit eyes caused "coagulation of the epithelium, but the cornea recovered within six days." Since oxalic acid is readily soluble in water, the dust and mists of solutions of this material are treated as eye irritants for the purposes of this guideline. No quantitative information is available concerning the concentrations which 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**

At the time of publication of this guideline, no measurement method for oxalic acid 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 repeated or prolonged skin contact with oxalic acid or liquids containing oxalic acid.
- If employees' clothing may have become contaminated with oxalic acid or liquids containing oxalic acid, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with oxalic acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of oxalic acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the oxalic acid, the person performing the operation should be informed of oxalic acid's hazardous properties.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of oxalic acid or liquids containing oxalic acid contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to oxalic acid or liquids containing oxalic acid, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with oxalic acid should be promptly washed or showered to remove any oxalic acid.
- Eating and smoking should not be permitted in areas where oxalic acid or liquids containing oxalic acid are handled, processed, or stored.
- Employees who handle oxalic acid or liquids containing oxalic acid 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 oxalic acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in metal cleaning and polishing operations for automobile radiators, boilers, and railroad cars to remove carbonaceous deposits from steel	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in textile cleaning and bleaching operations for rust, ink, and stain; bleaching of cotton and other fabrics; removal of discoloration from bleeding dyes; use as a sour in treatment of woolen and other piece goods; use in stripping and finishing operations in textile manufacture	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in bleaching and tanning of hides in leather manufacture	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during miscellaneous bleaching operations of wood, rosin, and cork	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of household and industrial cleaning and bleaching agents for metal and wood cleaning, cleaning preparations, disinfectants, and wax and grease removal	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in metallurgical processing of tin and extraction and purification of rare earth and actinide metals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in synthesis of other chemicals for manufacture of dyes, blue-print photography, and acids and starch hydrolysis	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in extraction and purification operations for chemicals, natural gums, and tall oil	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in lithography and photoengraving operations; use as an analytical reagent; use in manufacture of inks and lacquers; and in synthesis of pharmaceuticals	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 oxalic acid or liquids containing oxalic acid 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 oxalic acid or liquids containing oxalic acid get on the skin, promptly flush the contaminated skin with water. If oxalic acid or liquids containing oxalic acid penetrate 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 oxalic acid, 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 oxalic acid or liquids containing oxalic acid have been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the oxalic acid. 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 DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If oxalic acid 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:

Oxalic acid may be disposed of:

1. By making packages of oxalic acid in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. By dissolving oxalic acid in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR OXALIC ACID

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.
500 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 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 Health Guideline for Oxygen Difluoride

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: OF_2
- Synonyms: Difluorine monoxide; fluorine monoxide
- Appearance and odor: Colorless gas with a foul odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for oxygen difluoride is 0.05 part of oxygen difluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.1 milligram of oxygen difluoride per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Oxygen difluoride can affect the body if it is inhaled or if strong concentrations of oxygen difluoride gas contact the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of oxygen difluoride has produced severe headaches in humans. Although there are no reports regarding the effects of exposure to this chemical on the eyes or skin of humans, it would be expected that contact of the gas under pressure with the eyes or skin would cause burns. In animal experiments, inhalation of oxygen difluoride has caused tearing, shortness of breath, muscular weakness, vomiting, severe breathing difficulties (which are sometimes delayed in onset), and death.

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 oxygen difluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to oxygen difluoride 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 and eyes should be stressed.

—14" x 17" chest roentgenogram: Oxygen difluoride causes lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Oxygen difluoride is a severe pulmonary 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 by signs and symptoms of respiratory disease.

- **Summary of toxicology**

Oxygen difluoride gas is a severe respiratory irritant. In monkeys and dogs, the LC50 was 26 ppm for 60 minutes; signs of toxicity were lacrimation, dyspnea, muscular weakness, and vomiting; at autopsy, massive pulmonary edema and hemorrhage were observed. In mice, exposure to a low concentration (1 ppm for 60 minutes) produced tolerance to subsequent exposures 8 days later at levels which would otherwise have been fatal (4.25 ppm for 60 minutes). In humans, inhalation of the gas at fractions of a ppm produced intractable headache. Although there are no reports of effects on the eyes or skin of humans, it would be expected that

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 gas under pressure impinging upon the eyes or skin would produce serious burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 54

2. Boiling point (760 mm Hg): −145 C (−229 F)

3. Specific gravity (water = 1): 1.5 (liquid at boiling point)

4. Vapor density (air = 1 at boiling point of oxygen difluoride): 1.86

5. Melting point: −224 C (−371 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): 0.02 (reacts slowly)

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures greater than 250 C (482 F) will cause oxygen difluoride to decompose and cause pressure increases in cylinders.

2. Incompatibilities: Contact with all combustible materials, chlorine, bromine, iodine, platinum, and many other metals, metal oxides, and moist air may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride and carbon monoxide) may be released when oxygen difluoride decomposes.

4. Special precautions: Oxygen difluoride 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, but strong oxidizing agent

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor of oxygen difluoride can be detected by some persons at 0.1 ppm and by most at 0.5 ppm. The odor, however, may not be relied upon for warning purposes, as it is not characteristic and because olfactory fatigue develops rapidly."

2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "no signs of irritation of the external mucosa of the eye were observed in rats subjected to the lethal exposure of 15 ppm oxygen difluoride for 15 minutes."

3. Evaluation of Warning Properties: Since the *Hygienic Guide* points out that "olfactory fatigue develops rapidly" upon exposure to oxygen difluoride, and since no other quantitative information is available relating its warning properties to air concentrations, this gas 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 oxygen difluoride 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 oxygen difluoride may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during use as an oxidizer in rocket propellants	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 strong concentrations of oxygen difluoride gas get into the eyes, wash eyes immediately with large

amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately.

• **Skin Exposure**

If strong concentrations of oxygen difluoride gas get on the skin, immediately wash the skin with large quantities of water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of oxygen difluoride, 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 oxygen difluoride 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 with a mixed solution of caustic soda and slaked lime.

REFERENCES

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RESPIRATORY PROTECTION FOR OXYGEN DIFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 0.05 ppm
Gas Concentration	
0.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 0.5 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-oxidizable sorbents and providing protection against oxygen difluoride.*** 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 oxygen difluoride; 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 0.5 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

***Oxygen difluoride is an strong oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore should not be used to provide protection against oxygen difluoride. Only non-oxidizable sorbents should be used.

Occupational Health Guideline for Ozone

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: O_3
- Synonyms: None
- Appearance and odor: Colorless gas with a sharp, characteristic odor; it can be smelled at concentrations below the permissible exposure level.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ozone is 0.1 part of ozone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of ozone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ozone affects the body by being inhaled or by irritating the eyes, nose, and throat.

- **Effects of overexposure**

When a person is exposed to very low concentrations of ozone for even a brief period of time, the person may notice a sharp, irritating odor. As the concentration of ozone increases, the ability to smell it may decrease. Irritation of the eyes, dryness of the nose and throat, and cough may be experienced. If the ozone concentration continues to rise, more severe symptoms may develop. These may include headache, upset stomach, or vomiting, pain or tightness in the chest, shortness of breath or tiredness, which may last for several days to weeks. Finally, with higher levels of exposure, the lungs may be damaged and death 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 ozone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ozone 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 and lungs should be stressed.

—14" x 17" chest roentgenogram: Ozone may cause lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ozone 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.

- **Summary of toxicology**

Ozone is extremely irritating to the upper and lower respiratory tract. The characteristic odor is readily detectable at low concentrations (0.01 ppm to 0.05 ppm). Ozone produces local irritation of the eyes and mucous membranes and may cause pulmonary edema at high exposure. Systemically, ozone has been reported to mimic the effects of ionizing radiation, and may cause damage to chromosomal structures. A partial tolerance appears to develop with repeated exposures. Although most effects are acute, the possibility of chronic lung impairment should be considered, based upon animal experimentation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

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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1. Molecular weight: 48
2. Boiling point (760 mm Hg): −112 C (−169.6 F)
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of ozone): 1.65
5. Melting point: −192 C (−313 F)
6. Vapor pressure at 20 C (68 F): Not applicable
7. Solubility in water, g/100 g water at 20 C (68 F): 0.00003 (3 ppm)
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Ozone spontaneously decomposes under all ordinary conditions, so that it is not encountered except in the immediate vicinity of where it was formed. The decomposition is speeded by solid surfaces and by many chemical substances.
2. Incompatibilities: Ozone is a powerful oxidizing agent and reacts with all oxidizable materials, both organic and inorganic. Some reaction products are highly explosive.
3. Hazardous decomposition products: None
4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Use large amounts of water spray.

• **Warning properties**

1. Odor Threshold: Both Summer and May report an odor threshold for ozone of 0.1 ppm.
2. Irritation Levels: Grant reports that "at concentrations greater than 1 ppm in air, ozone has been found irritating to the eyes and nose and injurious to the respiratory tract. Concentrations of 2 to 3.7 ppm caused sensation of irritation to normal human eyes within 6 minutes."
3. Evaluation of Warning Properties: Since the odor threshold of ozone is at 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**

Sampling and analyses may be performed by collection of ozone in an impinger containing potassium iodide in sodium hydroxide, followed by treatment with phosphoric-sulfamic acid reagent, and spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ozone may be used. An analytical method for ozone 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.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ozone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during welding operations with inert gas-shielded arc welding devices	Local exhaust ventilation; canister respirator; shielding (to block rays)
Liberation during welding operations with argon-shielded, bare-wire arc welding (especially stainless steel, aluminum, and aluminum alloy containing silicon)	Large-volume local exhaust; general dilution ventilation; direct fresh air supply; shielding (to block rays)
Liberation during arc welding operations in confined spaces	Direct fresh air supply
Liberation during production of ozone	Process enclosure; local exhaust ventilation

Operation	Controls
Liberation during oxidizing process of fine organic chemicals production (primarily ozolaic acid)	Process enclosure; local exhaust ventilation
Liberation during operations involving high-intensity ultraviolet light (plasma torch operations, glass blowing, hot metal operations, photoengraving operations, and use of mercury vapor lamps, direct copying machines, and projecting equipment)	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during operations involving high-voltage electrical equipment (spectrographic and fluorometric apparatus, electroplating operations, high-volt linear accelerators, and electrostatic precipitators)	Local exhaust ventilation
Liberation during operations involving ozonizing process in treatment of water, industrial waste, and sewage; during air purification	Local exhaust ventilation; process enclosure; respiratory protective equipment
Liberation during drilling, cutting, and welding operations utilizing laser radiation	Local exhaust or general dilution ventilation
Liberaton during bleaching operations (textiles, paper, pulp, waxes, starch, sugar, teflon, and synthetic fibers); during refining of mineral oils and their derivatives; during processing of perfumes, vanilin, amd camphor; during aging and drying operations (wood, wines, whiskies, varnishes, and printing inks)	Process enclosure; local exhaust ventilation
Liberation during food preserving operations for mold and bacteria control in food storage and deodorization	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 ozone 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.

- **Breathing**

If a person breathes in large amounts of ozone, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. When breathing is difficult, properly trained personnel may assist the affected person by administering 100% oxygen. 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 ozone is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas.

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RESPIRATORY PROTECTION FOR OZONE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Vapor Concentration	
1 ppm or less	Any chemical cartridge respirator with a cartridge(s) containing non-oxidizable sorbents and providing protection against ozone. Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) containing non-oxidizable sorbents and providing protection against ozone. A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against ozone. 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-oxidizable sorbents and providing protection against ozone. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Paraquat

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: (a) $C_{12}H_{14}N_2Cl_2$; (b) $C_{12}H_{14}N_2(CH_3SO_4)_2$
- Synonyms: (a) 1,1'-dimethyl-4,4'-bipyridinium dichloride; (b) 1,1'-dimethyl-4,4'-bipyridinium bis (methosulfate)
- Appearance and odor: Odorless, colorless solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for paraquat is 0.5 milligram of paraquat 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 paraquat a Threshold Limit Value of 0.1 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Paraquat 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 paraquat may cause irritation of the eyes, nose, throat, and skin. It may also cause nose bleeding and abnormalities or loss of fingernails. Exposure to mixtures of paraquat and a related compound, diquat, may cause serious and permanent injury to the eyes. Swallowing paraquat may cause burning in the mouth and throat, nausea, vomiting, abdominal pain, diarrhea, heart, kidney, and lung damage, and liver damage with 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 paraquat.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to paraquat 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 eyes, respiratory system, heart, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Paraquat causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Paraquat is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Urinalysis: Since kidney damage has been observed in humans exposed to paraquat, a urinalysis should be performed, including 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 paraquat, a profile of liver function should be obtained by using 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**

Paraquat as a mist or aerosol is an irritant of the eyes, mucous membranes, and skin. In rats exposed to aero-

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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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sols of paraquat, the LC50 for 6 hours was 1 mg/m@3@; death was delayed and resulted from pulmonary hemorrhage and edema. In a study of 30 workers spraying paraquat over a 12 week period, approximately 50% of them had minor irritation of the eyes or nose; 1 worker had an episode of epistaxis. Of 296 spray operators with skin exposure described as gross and prolonged, 55 had damaged fingernails; the most common lesion was transverse white bands of discoloration, but loss of nail surface, transverse ridging, gross deformity of the nail plate, and loss of nails also occurred. Paraquat is commonly combined in commercial herbicides with diquat, a related compound; in several instances the commercial preparations splashed in the eyes have caused serious injury. There have been loss of corneal and conjunctival epithelium, mild iritis, and residual corneal scarring. In contrast, in the eye of a rabbit, one drop of a 50% aqueous solution of pure paraquat caused slow development of mild conjunctival inflammation, and pure diquat proved even less irritating. Presumably the surfactants present in the commercial preparations are responsible for the severe eye injuries in humans. The results from injection or ingestion of paraquat are in marked contrast to the irritant effects usually encountered from occupational exposure. Intraperitoneal injection or oral administration to rats at doses which caused delayed death resulted in a peculiar proliferative lesion in the lung; there was alveolar, perivascular, and peribronchial edema, with cellular proliferation into the alveolar walls resulting in large solid areas of the lung with no air-containing cavities. There are several reports of fatal accidental ingestion by humans; in 2 cases, one person ingested about 114 ml of a 20% solution, while the other was believed to have taken only a mouthful of the liquid, most of which was rejected immediately; the former died after 7 days and the latter after 15 days. Initial symptoms included burning in the mouth and throat, nausea, vomiting, and abdominal pain with diarrhea. After 2 to 3 days, signs of liver and kidney toxicity developed including jaundice, oliguria, and albuminuria; there were E.C.G. changes suggesting toxic myocarditis with conduction defects. Shortly before death there was respiratory distress; at autopsy, findings in the lung included hemorrhage, edema, and massive solid areas which were airless owing to fibroblastic proliferation in the alveolar walls and elsewhere. There is no evidence that inhalation or skin absorption causes the rapid progressive pulmonary fibrosis and injury to the heart, liver, and kidneys occurring from ingestion.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: (a) 257.2; (b) 408
2. Boiling point (760 mm Hg): Decomposes at 175–180 C (347–356 F)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of paraquat): 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): Very soluble
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, oxides of nitrogen and sulfur, and carbon monoxide) may be released when paraquat decomposes.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Grant states that "in tests on rabbit eyes pure paraquat at 50% concentration caused only mild superficial inflammation, developing in twelve hours and clearing in two to four days with no damage to the cornea."

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 paraquat 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 Enforce-

ment 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 paraquat or solutions containing paraquat, where skin contact may occur.

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

• Where exposure of an employee's body to paraquat or solutions containing paraquat 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 paraquat should be removed immediately and not reworn until the paraquat is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where paraquat or solutions containing paraquat may contact the eyes.

SANITATION

• Skin that becomes contaminated with paraquat should be immediately washed or showered to remove any paraquat.

• Eating and smoking should not be permitted in areas where paraquat or solutions containing paraquat are handled, processed, or stored.

• Employees who handle paraquat or solutions containing paraquat 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 paraquat may occur and control methods which may be effective in each case:

Operation	Controls
Use as an agricultural herbicide, desiccant, defoliation agent during pre-harvest; use as an herbicide for non-agricultural purposes on highway margins, around commercial buildings; use to control aquatic weeds	Personal protective equipment
Manufacture, formulation, and processing of paraquat and aqueous solutions of the salts	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 paraquat or solutions containing paraquat 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 paraquat or solutions containing paraquat get on the skin, immediately flush the contaminated skin with water. If paraquat or solutions containing paraquat 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 paraquat, 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 paraquat or solutions containing paraquat 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 paraquat 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 paraquat should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Paraquat may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR PARAQUAT

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate Concentration	
1.5 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.
Greater than 1.5 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 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 paraquat; 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 1.5 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Parathion

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: $(C_2H_5O)_2$ $PSOC_6H_4NO_2$
- Synonyms: O,O-Diethyl-O,p-nitrophenyl phosphorothioate; ethyl parathion
- Appearance and odor: Yellow to dark brown liquid with a characteristic odor, like garlic.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for parathion is 0.1 milligram of parathion per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 0.05 mg/m^3. The NIOSH Criteria Document for Parathion should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Parathion can affect the body if it is inhaled, comes in contact with the eyes or skin, or if swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: After inhalation of parathion, 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 parathion, 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 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 heartbeat, convulsions and coma may occur.

2. Long-term Exposure: Repeated exposure to parathion may make a person more susceptible to the effects of this and related chemicals. Repeated exposure 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 parathion.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to parathion 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, eyes, and attention to the cholinesterase levels in the blood should be stressed. The skin should be examined for evidence of chronic disorders.

—Cholinesterase determination: Parathion causes depressed levels of activity of cholinesterase in the serum and erythrocytes. The cholinesterase activity in the serum and erythrocytes should be determined by using

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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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. This test should be performed at four-week intervals, except for those employees in areas which may involve intense exposure, for whom the test should be repeated weekly. If any employee works with parathion more than 12 hours per day, he should be tested every 3 weeks. Employees should also be tested at any time overexposure is suspected or signs or symptoms of toxicity appear. Any employee having a 30 to 40% decrease in cholinesterase should be removed from exposure and placed under medical observation.

- **Summary of toxicology**

Parathion is an anticholinesterase agent; absorption may occur from inhalation of the vapor or mist, from skin absorption of the liquid, or from ingestion. 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 and skeletal and smooth muscle 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. A few drops of technical parathion in the eyes of animals have produced lacrimation and moderate conjunctivitis. The minimum lethal oral dose of parathion for humans has been estimated to range from less than 10 mg up to 120 mg. In a study of 115 workers exposed to parathion under varying conditions, the majority excreted significant amounts of p-nitrophenol (a metabolite of parathion) in the urine, while only those with heavier exposures had a measurable decrease in blood cholinesterase.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 291.3
2. Boiling point (760 mm Hg): 375 C (707 F) (calculated)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of parathion): Not applicable
5. Melting point: 6 C (43 F) (pure grade); 0 C (32 F) (technical grade)
6. Vapor pressure at 20 C (68 F): 0.0004 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): .00002
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 100 C (212 F) may cause decomposition so that containers burst.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, phosphorus, sulfur, and carbon monoxide) may be released when parathion decomposes.
4. Special precautions: Parathion will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The odor threshold of parathion is 0.04 ppm (American Society of Testing Materials Bulletin).
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "a few drops of technical parathion in animals has produced immediate blinking, lacrimation, and moderate conjunctivitis. Pupil constriction was also observed, with a return to normal size and reaction the following day. Eye contact with 1% aqueous suspensions of 15% wettable powders did not show evidence of irritation or other obvious reaction."
3. Evaluation of Warning Properties: Since the odor threshold of parathion is so low, parathion 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 parathion using a filter with subsequent recovery with iso-octane and gas chromatographic analysis. A detailed analytical method for parathion 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 T" (order number PB 262 404).

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 parathion.

• If employees' clothing has had any possibility of being contaminated with parathion, employees should change into uncontaminated clothing before leaving the work premises.

• Where there is any possibility of exposure of an employee's body to parathion, 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 parathion should be removed immediately and not reworn until the parathion is removed from the clothing.

• Clothing which has had any possibility of being contaminated with parathion should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of parathion from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the parathion, the person performing the operation should be informed of parathion's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid parathion contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to parathion, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with parathion should be immediately washed or showered with soap or mild detergent and water to remove any parathion.

• Workers subject to skin contact with parathion should wash with soap or mild detergent and water any areas of the body which may have contacted parathion at the end of each work day.

• Eating and smoking should not be permitted in areas where parathion is handled, processed, or stored.

• Employees who handle parathion 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 parathion may occur and control methods which may be effective in each case:

Operation	Controls
Application as a pesticide on agricultural crops, vegetables and ornamentals and on agricultural premises	Personal protective equipment
Formulation for use as an insecticide	Process enclosure; personal protective equipment
Manufacture of parathion	Process enclosure; 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 parathion or parathion 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 parathion or parathion mists get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If parathion or parathion 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 parathion, 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 parathion 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 parathion 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:

Parathion 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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RESPIRATORY PROTECTION FOR PARATHION

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate or Vapor Concentration	
1 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, fume, and mist filter(s), including pesticide respirators which meet the requirements of this class. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust, fume, and mist 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, fume, 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.
20 mg/m³ or less	A powered air-purifying respirator with an organic vapor cartridge and high efficiency particulate filter, including pesticide respirators which meet the requirements of this class. 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. 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 parathion; 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 Health Guideline for Pentaborane

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_5H_9
- Synonyms: Stable pentaborane, pentaboron anhydride
- Appearance and odor: Colorless liquid with a strong, pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pentaborane is 0.005 part of pentaborane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.01 milligram of pentaborane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pentaborane 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: Exposure to low concentrations of pentaborane may cause lightheadedness, drowsiness, nervousness, lack of coordination, and tremors. The onset of these symptoms may be delayed as long as 48 hours. After exposure to higher concentrations, the onset of symptoms may be prompt and may include the above symptoms plus spasms of the face, neck, arms, legs, and abdomen. After severe exposure, convulsions may occur. In animals impairment of liver and kidney function has been reported. Also, in animals, the vapor has caused severe irritation of the eyes and the liquid has caused inflammation of the skin.

2. Long-term Exposure: Prolonged exposure to low concentrations of pentaborane may cause headache, fatigue, drowsiness, the inability to concentrate, and the lack of coordination.

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 pentaborane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pentaborane 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, liver, and kidneys should be stressed. The skin and eyes 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**

Pentaborane vapor affects the nervous system and causes signs of both hyperexcitability and narcosis. Exposure of rats to 10 ppm for 2 hours was fatal; effects included weakness, incoordination, corneal opacities, tremors, and convulsions; other animal studies have indicated that kidney and liver damage may occur. In humans, the onset of symptoms may be delayed up to 48 hours after exposure; dizziness, headache, and drowsiness are common; other symptoms include fatigue, incoordination, and tremor. After exposure to higher concentrations, the onset of symptoms may be prompt and include tonic spasms of the muscles of the face,

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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neck, abdomen, and extremities; after severe exposures, convulsive seizures may occur. The results of exposure to animals for 60 minutes are: 8 ppm, some decrement in performance of learned tasks and slight signs of toxicity; 15 ppm, convulsions; 30 ppm, convulsions and death. Severe irritation and corneal opacity of the eyes of test animals occurred from exposure to the vapor; the liquid on the skin of animals caused acute inflammation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 63.1
2. Boiling point (760 mm Hg): 58.4 C (137 F)
3. Specific gravity (water = 1): 0.63
4. Vapor density (air = 1 at boiling point of pentaborane): 2.2
5. Melting point: −47 C (−52 F)
6. Vapor pressure at 20 C (68 F): 171 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts slowly to form hydrogen gas
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 150 C (302 F) cause decomposition and pressure buildup in containers.
2. Incompatibilities: Pentaborane reacts with oxidizers to form highly explosive mixtures. Contact with halogens or halogenated compounds may cause explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as boron acids) may be released in a fire involving pentaborane.
4. Special precautions: Pentaborane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 30 C (86 F) (closed cup when pure); impure material ignites spontaneously in air
2. Autoignition temperature: 35 C (95 F) (impure material ignites at lower temperatures)
3. Flammable limits in air, % by volume: Lower: 0.42; Upper: Not obtainable
4. Extinguishant: Let small fires burn. Water spray, foam, dry chemical, and carbon dioxide will decrease intensity of large fires. Do not use halogenated extinguishing fluids.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that pentaborane has a characteristic odor, but that it is "not a reliable index of exposure." According to a technical bulletin from Callery Chemical Company, the median detectable concentration of pentaborane by odor is 2.5 mg/m@3@, which is many times greater than the permissible exposure limit.
2. Eye Irritation Level: Pentaborane vapor is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold is many times greater than the permissible exposure limit of pentaborane, and since there is no other quantitative information relating warning properties to air concentrations of pentaborane, 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**

At the time of publication of this guideline, no measurement method for pentaborane 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 skin contact with liquid pentaborane, where skin contact may occur.
- Clothing wet with liquid pentaborane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pentaborane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pentaborane, the person performing the operation should be informed of pentaborane's hazardous properties.

• Where exposure of an employee's body to liquid pentaborane 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 liquid pentaborane should be removed immediately and not reworn until the pentaborane 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 pentaborane contacting the eyes.
• Where there is any possibility that employees' eyes may be exposed to liquid pentaborane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes wet with liquid pentaborane should be immediately washed or showered with soap or mild detergent and water to remove any pentaborane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to pentaborane may occur and control methods which may be effective in each case:

Operation	Controls
Use in chemical research as jet and rocket fuels, catalysts, corrosion inhibitor-fluxing agents, and oxygen scavengers	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a chemical intermediate (higher boranes, alkyl boranes— ethyl pentaborane and various hydrides); these are not industrial chemicals	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 pentaborane or strong concentrations of pentaborane 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 promptly. Contact lenses should not be worn when working with this chemical.
• **Skin Exposure**
If liquid pentaborane or strong concentrations of pentaborane vapor get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid pentaborane or strong concentrations of pentaborane vapor 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 pentaborane, 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 pentaborane 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 pentaborane 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. Pentaborane 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 pentaborane vapors are permitted.
• Waste disposal method:
Pentaborane 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 PENTABORANE

Condition	Minimum Respiratory Protection* Required Above 0.005 ppm
Vapor Concentration	
0.05 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
0.25 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 3 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 pentaborane. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Pentachloronaphthalene

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: $C_{10}H_3Cl_5$
- Synonyms: Halowax 1013
- Appearance and odor: Pale, yellow solid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pentachloronaphthalene is 0.5 milligram of pentachloronaphthalene per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pentachloronaphthalene can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. Every effort should be made to prevent skin, eye, oral, or inhalation contact with this material.

- **Effects of overexposure**

Overexposure to pentachloronaphthalene causes headache and dizziness. Prolonged overexposure to pentachloronaphthalene may cause an acne-like skin rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, yellow jaundice, and possibly 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 pentachloronaphthalene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pentachloronaphthalene 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: Pentachloronaphthalene may cause liver damage. A profile of liver function should be performed by using 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**

Pentachloronaphthalene is a severe hepatic toxin, with marked effects upon the skin. While a solid at room temperature, the heated liquid produces a hazardous vapor. Rats exposed to the vapor of a mixture of hexa- and pentachloronaphthalene at average concentrations of 1.16 mg/m^3 for 16 hours daily up to 4-½ months showed definite liver injury, while 8.8 mg/m^3 produced some mortality and severe liver injury. The most striking human response to prolonged skin contact with the solid, or to shorter term inhalation of hot vapors, is chloracne. This is an acne-form skin eruption characterized by papules, large comedones and pustules, chiefly affecting the face, neck, arms, and legs. Pruritic erythematous and vasculoerythematous reactions have also been reported. Skin lesions are often accompanied by symptoms of systemic effects, including headache, vertigo, and anorexia. Liver damage characterized by toxic jaundice, which may progress to fatal hepatic necrosis, results from the inhalation of higher concentrations of the hot fumes of the molten substance. Skin absorption

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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has been demonstrated in animals and is suspected in man.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 300.5
2. Boiling point (760 mm Hg): 327 to 371 C (620 to 700 F)
3. Specific gravity (water = 1): 1.67
4. Vapor density (air = 1 at boiling point of pentachloronaphthalene): 10.4
5. Melting point: 120 C (248 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: 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 and toxic chloride fumes) may be released in a fire involving pentachloronaphthalene.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "eye injury has not proved to be troublesome with the chloronaphthalenes;" nonetheless, they specifically state that "if respirators are used, they should be of the full-facepiece type approved by the U. S. Bureau of Mines for disperoids or organic vapors."
3. Evaluation of Warning Properties: There are no quantitative data relating warning properties to air concentrations of pentachloronaphthalene; therefore, 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 pentachloronaphthalene with a filter and a bubbler containing iso-octane, followed by gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure pentachloronaphthalene may be used. An analytical method for pentachloronaphthalene 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 molten pentachloronaphthalene.
- 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 pentachloronaphthalene or liquids containing pentachloronaphthalene.
- 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 pentachloronaphthalene vapors from the heated material.
- If employees' clothing may have become contaminated with solid pentachloronaphthalene, employees

should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with molten pentachloronaphthalene should be removed immediately and not reworn until the pentachloronaphthalene is removed from the clothing.

• Non-impervious clothing which becomes contaminated with solid pentachloronaphthalene or liquids containing pentachloronaphthalene should be removed promptly and not reworn until the pentachloronaphthalene is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten pentachloronaphthalene contacting the eyes.

• Employees should be provided with and required to use splash-proof safety goggles where solid pentachloronaphthalene or liquids containing pentachloronaphthalene may contact the eyes.

SANITATION

• Workers subject to skin contact with pentachloronaphthalene should wash with soap or mild detergent and water any areas of the body which may have contacted pentachloronaphthalene at the end of each work day.

• Skin that becomes contaminated with pentachloronaphthalene should be promptly washed or showered with soap or mild detergent and water to remove any pentachloronaphthalene.

• Eating and smoking should not be permitted in areas where solid pentachloronaphthalene is handled, processed, or stored.

• Employees who handle solid pentachloronaphthalene or liquids containing pentachloronaphthalene 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 pentachloronaphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture of electric equipment as an insulating material; pouring molten solvent or finely ground solid materials; dipping; peeling and covering insulated cable with fabric	Local exhaust ventilation; general dilution with intake and exhaust fans; personal protective equipment
Liberation from use of electrical equipment insulated with octachloronaphthalene/ pentachloronaphthalene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an inert compound of resins or polymers for coating or impregnating textiles, wood, and paper to impart flame resistance, water proofness, and fungicidal and insecticidal properties	Process enclosure; local exhaust ventilation; general dilution with intake and exhaust fans; personal protective equipment
Use as an additive for cutting oil in various operations performed on metals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an additive to special lubricants in crankcase oil, lubricants for farm machinery, and extreme-pressure lubricants	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 solid pentachloronaphthalene or liquids containing pentachloronaphthalene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. If molten pentachloronaphthalene gets into the eyes, immediately flush the eyes with large amounts of water to remove heat. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If non-impervious clothing becomes contaminated with pentachloronaphthalene, remove and clean the clothing before wearing again.If non-impervious clothing becomes heavily contaminated, it should be destroyed. If solid pentachloronaphthalene or liquids containing

pentachloronaphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If irritation persists after washing, get medical attention. If molten pentachloronaphthalene gets on the skin or non-impervious clothing, immediately flush the affected area with large amounts of water to remove heat. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of pentachloronaphthalene, 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 pentachloronaphthalene 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 pentachloronaphthalene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing pentachloronaphthalene should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Pentachloronaphthalene may be disposed of in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Pentachloronaphthalene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR PENTACHLORONAPHTHALENE

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate Concentration	
5 mg/m³ or less	Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m³ or less	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.
1000 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 1000 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. 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 Pentachlorophenol

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_6Cl_5OH
- Synonyms: PCP; penta
- Appearance and odor: Light brown solid with a pungent odor when hot.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pentachlorophenol is 0.5 milligram of pentachlorophenol per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pentachlorophenol 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 pentachlorophenol may cause irritation of the eyes and respiratory tract. Bronchitis has been reported to occur. Systemic effects from either a large exposure or repeated smaller exposures include weakness, loss of appetite, nausea, vomiting, shortness of breath, chest pain, excessive sweating, headache, and dizziness. In fatal cases the temperature is often very high and death may occur as early as three hours after the onset of symptoms. The risk of serious intoxication is greater in hot weather. Persons with decreased liver or kidney functions are more susceptible to poisoning from this chemical. Repeated exposure to pentachlorophenol may cause an acne-like skin rash and liver damage. Commercial pentachlorophenol may be contaminated with dioxin compounds which are much more toxic than pentachlorophenol.

- **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 pentachlorophenol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pentachlorophenol 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 cardiovascular system, eyes, upper respiratory tract, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders. Analysis of the urine for pentachlorophenol may be helpful in estimating the extent of absorption.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Pentachlorophenol dust and mist cause irritation of the eyes and upper respiratory tract; absorption results in an increase in metabolic rate and hyperpyrexia; prolonged skin exposure causes an acneform dermatitis. Human exposure to dust or mist concentrations greater than 1 mg/m^3 causes pain in the nose and throat, violent sneezing, and cough; 0.3 mg/m^3 may cause some nose irritation; persons acclimated to pentachlorophenol can tolerate concentrations up to 2.4 mg/m^3. Pentachlorophenol readily penetrates the skin; systemic intoxication is cumulative and has been fatal. Intoxication is characterized by weakness, anorexia, weight loss, and profuse sweating; there also may be headache, dizziness, nausea, vomiting, dyspnea, and chest pain. In fatal cases, the body temperature is frequently extremely high and

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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death has occurred as early as 3 hours after the onset of symptoms. The risk of serious intoxication is increased during hot weather; persons with impaired liver or kidney function are more susceptible to the effects of pentachlorophenol. The dust, mist, and vapor cause eye irritation. Prolonged exposure of workers has caused an acneform dermatitis; 10 workers engaged in production of pentachlorophenol for 5 to 10 months developed a widely disseminated skin eruption characterized by small and large furuncles, brown pigmentation, and some cicatrization; 7 workers also developed severe bronchitis; all but 1 worker still showed signs of extensive acne more than a year after cessation of exposure, and 4 still complained of bronchitis. On the skin, solutions of pentachlorophenol as dilute as 1% may cause irritation if contact is repeated or prolonged.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 266.3
  2. Boiling point (760 mm Hg): 311 C (592 F) (decomposes)
  3. Specific gravity (water = 1): 2.0
  4. Vapor density (air = 1 at boiling point of pentachlorophenol): Not applicable
  5. Melting point: 182– 190 C (360– 374 F)
  6. Vapor pressure at 20 C (68 F): 0.00017 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.002
  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, chlorinated phenols, and carbon monoxide) may be released when pentachlorophenol decomposes.
  4. Special precautions: None.
- **Flammability**
  1. Not combustible
- **Warning properties**
  1. Odor Threshold: The AIHA *Hygienic Guide* states that pentachlorophenol has a characteristic odor. No quantitative information is available, however, concerning the odor threshold of this substance.
  2. Irritation Levels: The *Documentation of TLV's* states that "dusts are particularly irritating to the eyes and nose, in concentrations appreciably greater than 1 mg/m^3, but some irritation of the nose may occur at 0.3 mg/m^3. Hardened workers can tolerate up to 2.4 mg/m^3."
  3. Evaluation of Warning Properties: Through its irritant effects, pentachlorophenol can be detected within three times of the permissible exposure limit. For the purposes of this guideline, therefore, pentachlorophenol 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 pentachlorophenol 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).

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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 pentachlorophenol or liquids containing pentachlorophenol.
- If employees' clothing has had any possibility of being contaminated with pentachlorophenol or liquids containing pentachlorophenol, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with pentachlorophenol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pentachlorophenol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pentachlorophenol, the person performing the operation should be informed of pentachlorophenol's hazardous properties.

• Where there is any possibility of exposure of an employee's body to pentachlorophenol or liquids containing pentachlorophenol, 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 pentachlorophenol should be removed immediately and not reworn until the pentachlorophenol 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 pentachlorophenol or liquids containing pentachlorophenol contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to pentachlorophenol or liquids containing pentachlorophenol, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with pentachlorophenol should be immediately washed or showered with soap or mild detergent and water to remove any pentachlorophenol.

• Workers subject to skin contact with pentachlorophenol or liquids containing pentachlorophenol should wash with soap or mild detergent and water any areas of the body which may have contacted pentachlorophenol at the end of each work day.

• Eating and smoking should not be permitted in areas where pentachlorophenol or liquids containing pentachlorophenol are handled, processed, or stored.

• Employees who handle pentachlorophenol or liquids containing pentachlorophenol 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 pentachlorophenol may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of preservatives, pesticides, and fungicides	Process enclosure; local exhaust ventilation; personal protective equipment
Application as a preservative for wood, starch, paint, adhesives, leather, latex, and oils; use in slime-algae control; use as a pesticide, herbicide, and snail control agent	Personal protective equipment
Manufacture of pentachlorophenol	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 pentachlorophenol or liquids containing pentachlorophenol 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 pentachlorophenol or liquids containing pentachlorophenol get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If pentachlorophenol or liquids containing pentachlorophenol penetrate through the clothing, remove the clothing immediately 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 pentachlorophenol, 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 pentachlorophenol or liquids containing pentachlorophenol 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 pentachlorophenol 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 depost in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing pentachlorophenol should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Pentachlorophenol may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Pentachlorophenol," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR PENTACHLOROPHENOL

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m³
Particulate or Vapor Concentration	
2.5 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust, fume, 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	Any chemical cartridge respirator with a full facepiece, an organic vapor cartridge(s), and dust, fume, and mist 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, fume, 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.

150 mg/m³ or less

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Pentane

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_{12}
- Synonyms: Normal pentane
- Appearance and odor: Colorless liquid with a gasoline-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pentane is 1000 parts of pentane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2950 milligrams of pentane per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 120 ppm (350 mg/m^3) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 610 ppm (1,800 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for Alkanes should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pentane can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to pentane may cause drowsiness and irritation of the eyes and nose. Greater exposure may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure 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 pentane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pentane 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 employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems and the skin should be stressed.

—Skin disease: Pentane is a skin 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 pentane 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 pentane 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 pentane might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: The aforementioned examinations should be performed on an annual basis.

- **Summary of toxicology**

Pentane vapor is a mild narcotic and mucous membrane irritant. Exposure to 90,000 to 120,000 ppm resulted in narcosis in animals in 5 to 6 minutes; 130,000 ppm was fatal, with respiratory arrest occurring within 5 minutes of the start of exposure. Pentane injected subcutaneous-

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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ly in rats produced temporary impairment of liver function and moderate neutropenia. While other aliphatic hydrocarbons produce drowsiness and mild irritation of the eyes and nose in human subjects, no symptoms resulted from exposure to pentane vapor for 10 minutes at 5000 ppm. Repeated or prolonged skin contact results in drying and cracking due to defatting action. No chronic systemic effects have been reported in humans. Aspiration may cause chemical pneumonia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 72.2
  2. Boiling point (760 mm Hg): 36 C (97 F)
  3. Specific gravity (water = 1): 0.63
  4. Vapor density (air = 1 at boiling point of pentane): 2.5
  5. Melting point: −129 C (−200 F)
  6. Vapor pressure at 20 C (68 F): 426 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.04
  8. Evaporation rate (butyl acetate = 1): 28.6
- **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 pentane.
  4. Special precautions: Pentane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −49 C (−57 F) (closed cup)
  2. Autoignition temperature: 260 C (500 F)
  3. Flammable limits in air, % by volume: Lower: 1.5; Upper: 7.8
  4. Extinguishant: Foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: May reports an odor threshold of 2.2 ppm. The *Hygienic Guide* states that "the odor threshold of pentane vapor is approximately the same as the recommended maximal concentration of 1000 ppm."
  2. Eye Irritation Level: Pentane is not a known eye irritant.
  3. Evaluation of Warning Properties: Since its odor threshold is at or below the permissible exposure limit, pentane is treated as a material with adequate 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 pentane. 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 pentane 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 pentane may be used. An analytical method for pentane 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 pentane.

• Any clothing which becomes wet with liquid pentane should be removed immediately and not reworn until the pentane is removed from the clothing.

• Clothing wet with liquid pentane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pentane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pentane, the person performing the operation should be informed of pentane's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where liquid pentane may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to pentane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes wet with liquid pentane should be promptly washed or showered with soap or mild detergent and water to remove any pentane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to pentane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a gasoline additive for automotive, aviation, and farm equipment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in synthesis of amyl chlorides for intermediates in manufacture of paint and lacquer solvents, tube oil additives, hydraulic fluids, pesticides, paint removers, solvent extenders, and miscellaneous petrochemicals; use in synthesis of polychlorocyclopentanes as intermediates in manufacture of fire-resistant polyester resins and paints, dye intermediates, insecticides, and plasticizers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a blowing agent for polymeric foams	Local exhaust ventilation; general dilution ventilation
Use as a raw material in synthesis of olefins for synthetic rubber and other petrochemicals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in solvent extraction processes; use as a general laboratory solvent; use as a medium solvent for polymerization reactions	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a component of lighter fluids and blow-torch fuel	Local exhaust ventilation; general dilution ventilation
Use as a heat-exchange medium in manufacture of artificial ice; use in manufacture of low-temperature thermometers; use in manufacture of polystyrene beads for styrofoam production	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 pentane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If pentane gets on the skin, promptly wash the contaminated skin with water. If pentane soaks through the clothing, remove the clothing immediately and wash the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of pentane, 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 pentane 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 pentane 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. Pentane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Pentane may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PENTANE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
5000 ppm or less	A gas mask with a chin-style or front- or back-mounted organic vapor canister. Any supplied-air respirator. Any self-contained breathing apparatus.
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.

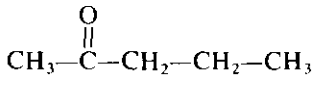
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR 2-PENTANONE

INTRODUCTION

This guideline summarizes pertinent information about 2-pentanone 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:** $C_5H_{10}O$
- **Structure:**



- **Synonyms:** Ethyl acetone, methyl n-propyl ketone, MPK
- **Identifiers:** CAS 107-87-9; RTECS SA7875000; DOT 1249, label required: "Flammable Liquid"
- **Appearance and odor:** Colorless liquid with a powerful, ethereal, fruity odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 86.15
2. Boiling point (at 760 mmHg): 102.3°C (216°F)
3. Specific gravity (water = 1): 0.81
4. Vapor density (air = 1 at boiling point of 2-pentanone): 3.0
5. Melting point: -77.5°C (-108°F)
6. Vapor pressure at 25°C (77°F): 16 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 4.3
8. Evaporation rate (butyl acetate = 1): 1.25
9. Saturation concentration in air (approximate) at 25°C (77°F): 2.1% (21,000 ppm)
10. Ionization potential: 9.37 eV

- **Reactivity**

1. Incompatibilities: Oxidizing agents may cause fires and explosions
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving 2-pentanone
3. Caution: 2-Pentanone will dissolve some plastics, resins, and rubber.

- **Flammability**

1. Flash point: 7.2°C (45°F) (closed cup)
2. Autoignition temperature: 452°C (846°F)
3. Flammable limits in air, % by volume: Lower, 1.6; Upper, 8.2
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: 11 ppm
2. Eye irritation levels: Humans exposed to 2-pentanone at 1,300 to 1,500 ppm found brief exposure severely irritating to the eyes, but no damage was produced.
3. Evaluation of warning properties for respirator selection: Because of its odor, 2-pentanone can be detected below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL); thus, 2-pentanone 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-pentanone is 200 parts of 2-pentanone per million parts of air (ppm) [700 milligrams per cubic meter of air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The NIOSH REL is 150 ppm (530 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 (700 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 250 ppm (875 mg/m³) (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 2-pentanone

	Exposure limits ppm	mg/m³
OSHA PEL TWA	200	700
NIOSH REL TWA	150	530
ACGIH TLV® TWA	200	700
STEL	250	875

HEALTH HAZARD INFORMATION

• **Routes of exposure**

2-Pentanone 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 2-pentanone by guinea pigs caused narcosis and congestion, hemorrhage, and edema of the lungs, liver, and kidneys.

2. *Effects on humans:* Acute inhalation of 2-pentanone has caused narcosis and central nervous system depression.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to 2-pentanone can cause headache, nausea, dizziness, vomiting, incoordination, and irritation of the eyes and respiratory passages.

2. *Long-term (chronic):* Dermal exposure to liquid 2-pentanone can cause 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 2-pentanone, 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-pentanone 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 2-pentanone. 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 2-pentanone 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 2-pentanone 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-pentanone may also be used if available. A detailed sampling and analytical method for 2-pentanone 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 2-pentanone.

Workers should be provided with and required to use splash-proof safety goggles where 2-pentanone may come in contact with the eyes.

SANITATION

Clothing which is contaminated with 2-pentanone 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-pentanone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of 2-pentanone'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-pentanone 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 of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle 2-pentanone 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-pentanone 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-pentanone

Operations	Controls
During application of cellulose- or resin-based coatings, finishes, and adhesives	Local exhaust ventilation, general dilution ventilation
During oven or air drying of coatings, finishes, and adhesives; during use in the manufacture of pharmaceuticals and some flavorings; during use as an extractant in dewaxing petroleum products	General dilution ventilation
During blending of raw materials for molded plastics	Local exhaust ventilation, personal protective equipment
During cleaning and maintenance of ketone-processing equipment	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-pentanone, an eye-wash fountain should be provided within the immediate work area for emergency use.

If 2-pentanone 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-pentanone, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If 2-pentanone gets on the skin, wash it immediately with soap and water. If 2-pentanone 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-pentanone 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-pentanone, 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-pentanone vapors. Burn the paper in a suitable location away from combustible materials.
4. Large quantities of liquids containing 2-pentanone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container. 2-Pentanone should not be allowed to enter a confined space such as a sewer because of the possibility of an explosion.
5. Liquids containing 2-pentanone 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 respirator 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 and meet other requirements of the decision logic may also be used.

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Table 3.—Respiratory protection for 2-petanone

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 1,000 ppm	Any chemical cartridge respirator with organic vapor cartridge(s) (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 1,500 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)
Less than or equal to 3,750 ppm	Any supplied-air respirator operated in continuous flow mode (substance reported to cause eye irritation or damage—may require eye protection)
Less than or equal to 5,000 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 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 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-equipment should be used.
†The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 150 ppm (530 mg/m³ (TWA).

Occupational Health Guideline for Perchloromethyl Mercaptan

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: CCl_3SCl
- Synonyms: PMM; trichloromethylsulfur chloride; trichloromethanethiol; perchloromethanethiol
- Appearance and odor: Pale yellow, oily liquid with a foul-smelling, strong acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for perchloromethyl mercaptan is 0.1 part of perchloromethyl mercaptan per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.8 milligram of perchloromethyl mercaptan per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Perchloromethyl mercaptan 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**

Inhalation of perchloromethyl mercaptan vapor may cause irritation of the eyes, nose, throat, and lungs as well as nausea. An exposure to this chemical by inhalation and skin contact has caused severe breathing difficulty and death. Liver and kidney damage also occurred following this exposure. The liquid splashed on the skin or in the eyes will cause 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 perchloromethyl mercaptan.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to perchloromethyl mercaptan 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 eyes, respiratory tract, 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 perchloromethyl mercaptan, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—14" x 17" chest roentgenogram: Perchloromethyl mercaptan causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Perchloromethyl mercaptan is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Liver function tests: Perchloromethyl mercaptan has been reported to cause liver damage in humans. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

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**

Perchloromethyl mercaptan vapor is a severe respiratory irritant and lacrimator. Mice and cats exposed for 15 minutes at 45 ppm died within 1 to 2 days from

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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pulmonary edema; 3-hour exposures at 9 ppm killed 50% of mice; repeated exposures over 3 months at 1 ppm resulted in the death of some mice. Eye irritation begins at 10 mg/m^3 (1.3 ppm). Exposure at higher concentrations causes marked irritation of the eyes, throat, and bronchi, as well as nausea. Three chemical workers were observed following accidental exposures to perchloromethyl mercaptan; two survived episodes of pulmonary edema, while the third died after 36 hours. The fatality resulted from a spill of the liquid on clothing and floor with exposure to the vapor. At autopsy, there was necrotizing tracheitis, massive hemorrhagic pulmonary edema, marked toxic nephrosis, and vacuolization of centrolobular hepatic cells. The liquid splashed on the skin may be expected to cause irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 185.9
2. Boiling point (760 mm Hg): 149 C (300 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of perchloromethyl mercaptan): 6.4
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 65 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble, reacts slowly to form hydrochloric acid, carbon dioxide, and sulfur.
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Perchloromethyl mercaptan decomposes at elevated temperatures to give carbon tetrachloride and sulfur monochloride. The decomposition is rapid at 149 C (300 F), the boiling point.
2. Incompatibilities: Contact with alkalies and amines may cause rapid decomposition. Contact with hot iron causes formation of toxic carbon tetrachloride vapor. Contact with hot water causes formation of hydrochloric acid, sulfur, and carbon dioxide.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon tetrachloride, sulfur monochloride, hydrogen chloride, sulfur dioxide, and carbon monoxide) may be released in a fire involving perchloromethyl mercaptan.
4. Special precautions: Perchloromethyl mercaptan will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: By analogy with other mercaptans, perchloromethyl mercaptan is assumed to have an odor threshold below the permissible exposure limit.

In addition, the following odor thresholds for different mercaptans can be found in May: n-butyl mercaptan, 0.00082 ppm; i-butyl mercaptan, 0.00054 ppm; i-pentyl mercaptan, 0.00021 ppm; i-amyl mercaptan, 0.00043 ppm; allyl mercaptan, 0.00005 ppm; crotyl mercaptan, 0.00016 and 0.000056 ppm; benzyl mercaptan, 0.0026 and 0.00035 ppm.

2. Eye Irritation Level: Grant states that perchloromethyl mercaptan "is a stink and tear gas that has been of military interest." No quantitative information is available, however, concerning the levels which produce eye discomfort.
3. Other Information: Grant states that this substance is a respiratory tract irritant.
4. Evaluation of Warning Properties: Since the odor threshold of perchloromethyl mercaptan is considerably below the permissible exposure limit and odor may be present within a properly functioning respirator, 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**

At the time of publication of this guideline, no measurement method for perchloromethyl mercaptan 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 repeated or prolonged skin contact with liquid perchloromethyl mercaptan.
• Clothing wet with perchloromethyl mercaptan should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of perchloromethyl mercaptan from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the perchloromethyl mercaptan, the person performing the operation should be informed of perchloromethyl mercaptan's hazardous properties.
• Non-impervious clothing which becomes wet with liquid perchloromethyl mercaptan should be removed promptly and not reworn until the perchloromethyl mercaptan is removed from the clothing.
• Employees should be provided with and required to use splash-proof safety goggles where liquid perchloromethyl mercaptan may contact the eyes.

SANITATION

• Skin that becomes wet with liquid perchloromethyl mercaptan should be promptly washed or showered with soap or mild detergent and water to remove any perchloromethyl mercaptan.
• Employees who handle liquid perchloromethyl mercaptan 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 perchloromethyl mercaptan may occur and control methods which may be effective in each case:

Operation	Controls
Use in chemical synthesis for agricultural and dye chemicals; use as an organic intermediate	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 perchloromethyl mercaptan or strong concentrations of perchloromethyl mercaptan vapors 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 perchloromethyl mercaptan gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid perchloromethyl mercaptan soaks 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 perchloromethyl mercaptan, 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 perchloromethyl mercaptan 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 perchloromethyl mercaptan 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 methods:
Perchloromethyl mercaptan 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 dissolving in a combustible solvent, such as alcohol, and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR PERCHLOROMETHYL MERCAPTAN

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Vapor Concentration	
1ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5ppm or less	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 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 Perchloryl Fluoride

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_3F
- Synonyms: None
- Appearance and odor: Colorless gas with a characteristic sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for perchloryl fluoride is 3 parts of perchloryl fluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 13.5 milligrams of perchloryl fluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Perchloryl fluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Perchloryl fluoride may cause respiratory irritation. The liquid, if allowed to remain in contact with the skin, may cause a burn. Animal exposures have produced severe breathing difficulties which have sometimes been delayed in onset. Also in animals, perchloryl fluoride can affect the ability of the blood to carry oxygen by forming methemoglobin. In man, methemoglobin formation may cause a bluish discoloration of the skin, drowsiness, dizziness, rapid heart beat, nausea, headache, shortness of breath, and unconsciousness.

- **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 perchloryl fluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to perchloryl fluoride 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 tract, blood, cardiovascular system, nervous system, and liver should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Perchloryl fluoride has been shown to cause methemoglobinemia in animals. Persons with blood disorders may be at increased risk from exposure. 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: Perchloryl fluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Perchloryl fluoride 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 other signs and symptoms of respiratory disease occur. Methemoglobin determinations should be performed if overexposure is suspected or signs and 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.

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**

Perchloryl fluoride gas is a respiratory irritant in humans and in animals causes the formation of methemoglobin. Dogs exposed to 450 ppm or 620 ppm for 4 hours developed hyperpnea, cyanosis, incoordination, and convulsions; methemoglobin levels were 29% and 71%, respectively. In dogs which died from exposure, there was lung damage consisting of alveolar collapse and hemorrhage; pigment deposition in the liver, spleen, and bone marrow was observed. Repeated exposure of three species of animals to 185 ppm for 7 weeks caused the death of more than half of them, guinea pigs being the most susceptible; all of the animals developed dyspnea, cyanosis, methemoglobinemia, alveolar edema, and pneumonitis. With similar repeated exposure of animals to 104 ppm for 6 weeks, the fluoride levels were increased by a factor of 20 to 30 in the blood, 5 to 8 in the urine, and 12 in the rat femur. One report states that workers suffered symptoms of upper respiratory irritation from brief exposure to unspecified concentrations. Perchloryl fluoride has the potential to form methemoglobin in man; the effects of methemoglobinemia are due to anoxia and include cyanosis, evident especially in the lips, nose, and earlobes; other effects are weakness, dizziness, and severe headache. The liquid is reported to produce moderately severe burns with prolonged skin contact.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 102.5
2. Boiling point (760 mm Hg): −46.7 C (−52 F)
3. Specific gravity (water = 1): 1.41 (liquid at 25 C)
4. Vapor density (air = 1 at boiling point of perchloryl fluoride): 3.5
5. Melting point: −146 C (−231 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): 0.06
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Containers may explode when heated above 500 C (932 F).
2. Incompatibilities: Contact with combustible materials, strong bases, amines, and finely divided metals may cause fires and explosions. Contact with readily oxidizable materials such as hydrogen sulfide, charcoal, sawdust, lampblack, etc. yields explosive products.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride and chlorine) may be released when perchloryl fluoride decomposes.
4. Special precautions: Perchloryl fluoride will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible by itself, but is a strong oxidizing agent
2. See 29 CFR 1910.101 for special regulations on storage of compressed gas cylinders.

• **Warning properties**

1. Odor Threshold: Sax states that the odor of perchloryl fluoride "can be detected as low as 10 ppm, although this cannot be relied upon as an indication of toxic concentrations in air."
2. Eye Irritation Level: Grant states that in industry "irritation of the eyes and nose has been reported when fluoride concentration has reached 5 mg/m^3 of air." Perchloryl fluoride is not specifically known to be an eye irritant.
3. Evaluation of Warning Properties: Since Sax notes that the odor "cannot be relied upon as an indication of toxic concentrations in air," and since there is no other quantitative information relating warning properties to air concentrations of perchloryl fluoride, this substance is treated like 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 perchloryl fluoride 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 the skin from becoming frozen from contact with liquid perchloryl fluoride or vessels containing liquid perchloryl fluoride.

• Non-impervious clothing which becomes contaminated with liquid perchloryl fluoride should be removed immediately and not reworn until the perchloryl fluoride has evaporated.

• Employees should be provided with and required to use splash-proof safety goggles where liquid perchloryl fluoride may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to perchloryl fluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a liquid oxidizer in rocket fuels, fuels used in cutting and welding, torches and chemical machinery	Process enclosure or adequate safety shields; local exhaust ventilation; personal protective equipment
Use in chemical synthesis in oxidation, ammonolysis, fluorination, perchlorylation, and etherification	Process enclosure or adequate safety shields; local exhaust ventilation; personal protective equipment
Use in flame photometry for analysis of different elements; miscellaneous uses for manufacture of fuel cells, gaseous dielectric for transformers, explosives, and metal processing	Process enclosure or adequate safety shields; 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.

• **Skin Exposure**

If liquid perchloryl fluoride gets on the skin, immediately flush the perchloryl fluoride from the contaminated skin. If liquid perchloryl fluoride penetrates 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 perchloryl fluoride, 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 perchloryl fluoride 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 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 PERCHLORYL FLUORIDE

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Vapor Concentration	
30 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
150 ppm or less	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 operated in pressure-demand or other positive pressure or continuous-flow mode and containing non-combustible sorbents.
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 containing non-combustible sorbents and providing protection against perchloryl fluoride. Any escape self-contained breathing apparatus.

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